Adsorption of Ethylene using Cobalt Oxide-Loaded Pillared Clay

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Highlights:

- Co-Al pillarization improves the quality of natural clays
- Pillared material features up to 114 m^2/g of the specific surface area
- Enhancement of ethylene adsorption up to 6 times was achieved

Abstract. Clay is an abundant material that is widely used as an adsorbent in pristine or pillared form. Pillared clays feature better properties, e.g. higher specific surface area, thus they can adsorb a higher quantity of adsorbates compared to pristine material. In this work, a preparation of pillared clay using Indonesian natural bentonite and its potential for ethylene removal are presented. The novelty is that a pillaring agent of cobalt (mixed with aluminum) was used, which not only served as a pillar but also as an active metal adsorbent for ethylene. Natural bentonite was pillared using Al $(NO_3)_3.9H_2O$ and Co $(NO_3)_2.6H_2O$. The resulting material was then calcined at 250 °C. The final material was characterized by N_2-sorption analysis, scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) analysis. The cobalt to aluminum ratios used were 1:9, 1:3, 1:1, 1:1/3, and 1:0. From characterization, the Co-Al pillared bentonite featured a specific surface area of up to 114 m^2/g (pristine bentonite = 42 m^2/g). In the adsorption test, an enhanced ethylene uptake of up to 6 times (at ambient temperature) compared to pristine bentonite was obtained. Thus, the results highlight the potential of cobalt oxide/pillared clay as ethylene scavenger.

Keywords: *adsorption; bentonite; cobalt oxide; ethylene; pillared clay.*

1 Introduction

Ethylene is a ripening hormone that can cause damage to fruits and vegetables during postharvest storage [1]. Overripeness in fruits and vegetables is not desirable and, unfortunately, the transportation process from farmer to consumer sometime takes a long time. Hence, certain treatments are needed so that fruits and vegetables are less easily damaged and their quality is maintained. Controlling ethylene can be performed by using an ethylene blocker (e.g. 1-

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methylcyclopropene (1-MCP) [2]), oxidator (e.g. $KMnO_4$ [3]), and adsorbent (e.g. acidified activated carbon powder-$PdCl_2$-$CuSO_4$ [4] and cobalt oxide-loaded carbon [5]). The ethylene blocker 1-MCP can prevent the ethylene reception in plants, but it is very expensive [2]. $KMnO_4$ is widely used as a commercial ethylene scavenger. However, after oxidizing ethylene, $KMnO_4$ is reduced to MnO_2 [3] so it cannot be recovered after being used to remove the ethylene. Activated carbon doped with active metals can be used as adsorbent. Cobalt oxide can be used as active site due to its strong affinity towards organic substances and it is relatively cheap [6,7]. However, using porous carbon as support is very costly, especially due to the high temperature heating involved in its manufacture [8].

The negative effects of ethylene can result in significant post-harvest losses of 10 to 80% [9]. Therefore, a study to produce a more economical and abundantly available ethylene remover is needed. Clay is an alternative adsorbent that can be used for this purpose [10]. Clay is an economical and easily obtainable material. So far clay has not been widely used, even though its potential and advantages are considerable. While being cheap and environmentally friendly, it can act as a superior adsorbent material due to its properties and structure. Thus, clay can be explored as an adsorbent raw material to increase its economic value. Clay is limitedly employed as an adsorbent to adsorb dye contaminants, e.g. methylene [11, 12] and basic blue [13].

Bentonite is a type of clay with a major content of smectite mineral (montmorillonite) at 85-95%. Montmorillonite has the ability to swell and to be intercalated with organic compounds. However, due to its low surface area, the adsorptive capacity of montmorillonite is limited, so it needs to be modified to improve its adsorption performance [14]. The added value of clay can be increased by intercalating a pillaring agent into the silicate clay layer to obtain pillared clay compound. The advantages of pillared clay compared to pristine clay are: higher thermal stability, greater pore volume and high specific surface area.

This study investigated the synthesis of cobalt oxide-loaded pillared clay and its application as ethylene adsorbent. Clay was explored and utilized as an ethylene adsorbent by adding a pillaring agent. The cobalt oxide-loaded pillared clay was obtained through bentonite pillarization with addition of metal salt as the pillaring agent. It is a novelty of this research that a pillaring agent of cobalt (mixed with aluminum) was used, not only to serve as a pillar but also as an active metal adsorbent for ethylene. The clay was calcined to maintain the structure of the clay and the pillar, so that pillared clay with a larger surface area could be obtained. This paper also describes the effects of cobalt's composition in the clay material as well as the pore structures of the clay on the ethylene adsorption capacity of the material.

2 Material and Methods

2.1 Material

The material used in this study consisted of main and supporting materials. Natural bentonite clay originating from Klaten, Central Java was used as the main material for preparation of the adsorbent. The metal salts aluminum nitrate nonahydrate (Al $(NO_3)_3.9H_2O$, 98.5% purity) and cobalt nitrate hexahydrate (Co $(NO_3)_2.6H_2O$, 99% purity) were used as pillaring agents. All materials were obtained from Merck, Germany. Ethylene gas used as adsorbate was obtained from PT Samator Gas Indonesia.

2.2 Methods

2.2.1 Material Synthesis

Pillarization of bentonite was conducted based on the method described in [15]. Hydration was carried out after pillarization by preparing a clay suspension consisting of 3 g of clay in 300 ml of water, after which the clay suspension was stirred at room temperature for 2 hours. In a separate vessel, pillaring agent was prepared by slowly adding 0.2 M NaOH solution to 0.2 M salt solution with an OH/metal ratio of 2. The mixture was then heated at 60 °C and stirred until homogeneous. The ratio of cobalt and aluminum salt was varied at 1:9, 1:3, 1:1, 1:1/3, and 1:0.

The pillaring agent solution was added to the clay suspension, stirring it for 2 hours at room temperature. After pillarization, the clay was separated from the filtrate using a vacuum pump and dried in an oven at 60 °C. The clay was removed from the oven and mashed, and then calcined at 250 °C for 3 hours under nitrogen flow. In the remainder of this paper, the samples are referred to by the name of the material followed by the pillaring agent ratio, e.g. pillared clay Co:Al 1:3 for the sample that was treated using a ratio of 1:3 Co:Al.

The pore structure of the pillared clay was evaluated by N_2-sorption analysis at 77 K (NOVA 2000, Quantrachrome). The specific surface area was calculated from the equilibrium data of nitrogen adsorption-desorption using the Brunauer-Emmet-Teller model (BET) with relative pressure (P/Po) between 0.05 and 0.30 [16]. The BET equation is shown in Eq. (1).

$$\frac{V}{V_m} = \frac{CP}{\left(P_o - P\right)\left[1 + \left(C-1\right)\left(\frac{P}{P_o}\right)\right]} \tag{1}$$

where V is the total volume of adsorbed gas, V_m is the monolayer coverage, P is the pressure, and C is a constant.

The structural morphology of the samples was analyzed by scanning electron microscope (SEM, JSM 6510 LA, JEOL). The samples were placed in a closed holder with a carbon layer and then analyzed using a secondary electron detector. The elemental composition of the samples was identified using an energy dispersive X-ray analyzer (EDX-8000, Shimadzu).

2.2.2 Adsorption Measurement of Ethylene

The obtained pillared clay was then employed to adsorb ethylene. The adsorption system was conditioned at ambient temperature (30 °C). Before performing adsorption, the system was evacuated to remove the gas from the adsorption rig. The ethylene was then dosed gradually from vacuum to 1 atm. Adsorption equilibrium was indicated by the stability of the pressure in the adsorption system. The pressure was detected using an installed pressure indicator. The adsorption equipment is shown in Figure 1.

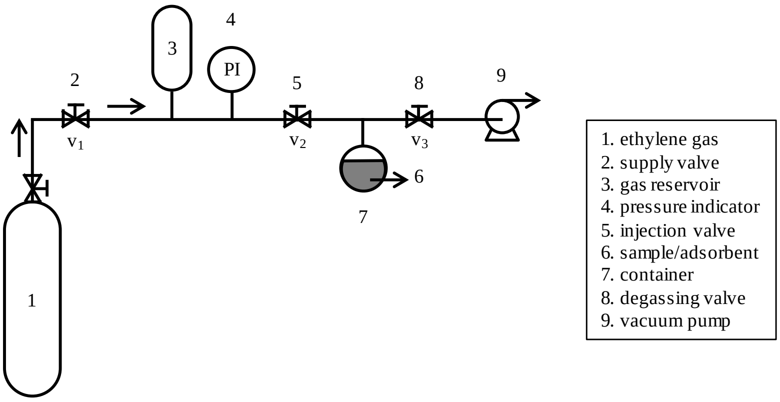


Figure 1 Scheme of adsorption rig to carry out adsorption measurements.

The relationship between ethylene uptake on the surface of the adsorbent and the amount of ethylene in the gas phase in equilibrium for a given temperature was determined. The data were evaluated using the equilibrium equation from the Toth model:

$$C_{\mu} = C_{\mu s} \frac{bP}{\left[1+\left(bP\right)^{t}\right]^{1/t}} \tag{2}$$

where C_{μ} is the ethylene concentration, $C_{\mu s}$ is the maximum ethylene concentration on the surface of the adsorbent, b is the equilibrium constant, P is the pressure, and t is the heterogeneity.

3 Results and Discussion

3.1 Material Characterizations

The existence of cobalt in bentonite is important for the success of the pillarization process. The presence of cobalt functions as pillaring agent was expected to increase the surface area of the bentonite along with active metals that can adsorb ethylene.

The greater active surface area of the adsorbent maximizes the adsorption process, so that the amount of ethylene uptake increases. Therefore, the existence of metals in the bentonite is important to determine. To see the metal contents in the bentonite, an EDX analysis was carried out.

Table 1 shows the results of the EDX analysis for the natural bentonite and the pillared bentonite with metals in oxide form. The major components of the natural bentonite were Si, Al, Ca and Fe compounds. In the pillared bentonite (Co:Al 1:1 and Co:Al 1:0), the amounts of Ca, Fe, K and Mn were lower than those in the natural bentonite. Accordingly, Co was present and with an increasing ratio of Co to Al, the amount of Co increased. This indicates that the pillaring process was successful.

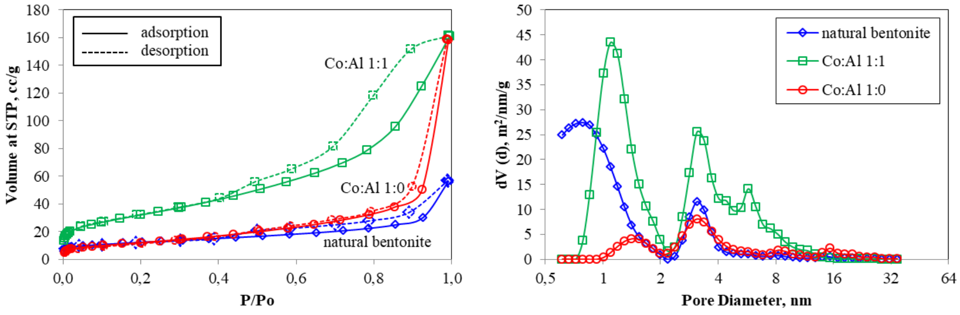
Table 1 Composition of bentonite and pillared bentonite.

Component	**Mass %**		
	Natural Bentonite	**Co:Al 1:1**	**Co:Al 1:0**
Al_2O_3	23.41	36.50	9.19
CaO	11.53	0.23	3.27
Co_2O_3	0.00	20.84	60.59
Fe_2O_3	5.17	3.94	2.40
K_2O	1.38	0.90	0.58
MnO	0.14	0.04	0.06
SiO_2	55.98	35.69	22.40
SO_3	1.52	1.35	1.28
TiO_2	0.57	0.40	0.24
others	0.31	0.10	0.00
	100.00	100.00	100.00

Porous materials have a different pore structure depending on the raw material used and the process conditions. Therefore, the material will have different characteristics related to its N_2 adsorption and desorption ability. The N_2 adsorption and desorption curves are the basis for determining the porous character of various materials. Figure 2 shows the N_2 physisorption of the samples. The N_2 adsorption-desorption curves show that meso/macropore structures were more dominant than micropore structures. This is indicated by the vertical line of the curve at relative pressure (P/Po) > 0.9.

All isotherms could be classified as type IV according to IUPAC classification. Within a certain pressure range, the desorption line does not coincide with the adsorption line, which is called a hysteresis loop. This is commonly associated with the presence of mesopores, a common feature of type IV isotherms [17].

The pore size distribution of the materials was studied using the Barrett, Joyner, and Halenda (BJH) method. From the pore size distribution, a detailed description of the micropore and mesopore regions of the materials was obtained. Figure 2(b) shows that the bentonite and the pillared bentonite had pore structures between 0 and 32 nm, with the highest peak located around 1 nm. In addition, it can be seen that the bentonite and the pillared bentonite featured major fractions of pore volume in the range of 2 to 22 nm, i.e. mesopores.



(a) (b)

Figure 2 (a) Adsorption and desorption of nitrogen in pristine bentonite and the pillared materials at Co:Al 1:1 and Co:Al 1:0. (b) The QSDFT-N2 pore size distribution of the materials.

The physical characteristics of the adsorbent affect the adsorption process. The intercalation and pillaring processes resulted in an increase of the surface area and the pore volume compared to the natural bentonite. The structural properties, i.e. specific surface area, average pore diameter and pore volume, are presented in Table 2. From this table it can be seen that the pillared clay possessed a mesoporous structure. This can be seen from the mesopore areas and volumes, which were more dominant than micropore areas and volumes. According to the IUPAC classification, mesopores are pores in solids with a size of 2 to 50 nm, while micropores are pores in solids with a size <2 nm [16].

The pillared bentonite Co:Al 1:1 had the largest surface area (114 m^2/g), almost three times larger than the natural bentonite (42 m^2/g), as shown in Table 2. The Co:Al had an average pore diameter of 8.7 nm, which is in the mesopore range. Pillarization also occurred in Co:Al 1:3 and Co:Al 1:1/3, affecting an increase of the surface areas (two times compared to the pristine bentonite). In Co:Al 1:0 only a slight increase in surface area was seen, which is likely due to the weight of the Co atoms increasing the total mass of the material.

Scanning electron microscopy (SEM) is an analysis that can illustrate the condition of the outer surface of a material. Figure 3 contains SEM images that show the structural morphologies of the materials. The addition of cobalt caused a morphological change in the materials.

Natural bentonite has a layered structure. The pillared bentonite Co:Al 1:3 was successfully intercalated. In the pillared bentonite Co:Al 1:3, the space between the layers became greater and stronger, yet it seems that the pillared bentonite Co:Al 1:0 became more fragile, probably because of the high cobalt content. Therefore, further study is necessary to know the maximum cobalt content to prevent accumulation or agglomeration of cobalt in the bentonite.

Table 2 Characteristics of clay and pillared clay.

Characteristics	**Natural Bentonite**	**Pillared Clay**				
		Co:Al 1:9	**Co:Al 1:3**	**Co:Al 1:1**	**Co:Al 1:1/3**	**Co:Al 1:0**
Surface area (S_{BET}), m^2/g	42.40	59.70	96.61	114.50	92.76	43.98
Mesopore area (S_{meso}), m^2/g	40.62	45.89	60.03	114.50	92.76	43.98
$\%S_{meso}$	95.81	76.87	62.14	100.00	100.00	100.00
Total pore volume, cm^3/g	0.09	0.10	0.11	0.25	0.37	0.24
Mesopore volume (V_{meso}), cm^3/g	0.09	0.09	0.09	0.25	0.37	0.24
$\%V_{meso}$	98.85	93.88	83.20	100.00	100.00	100.00
Average pore diameter, nm	8.19	6.57	4.68	8.71	15.92	22.26

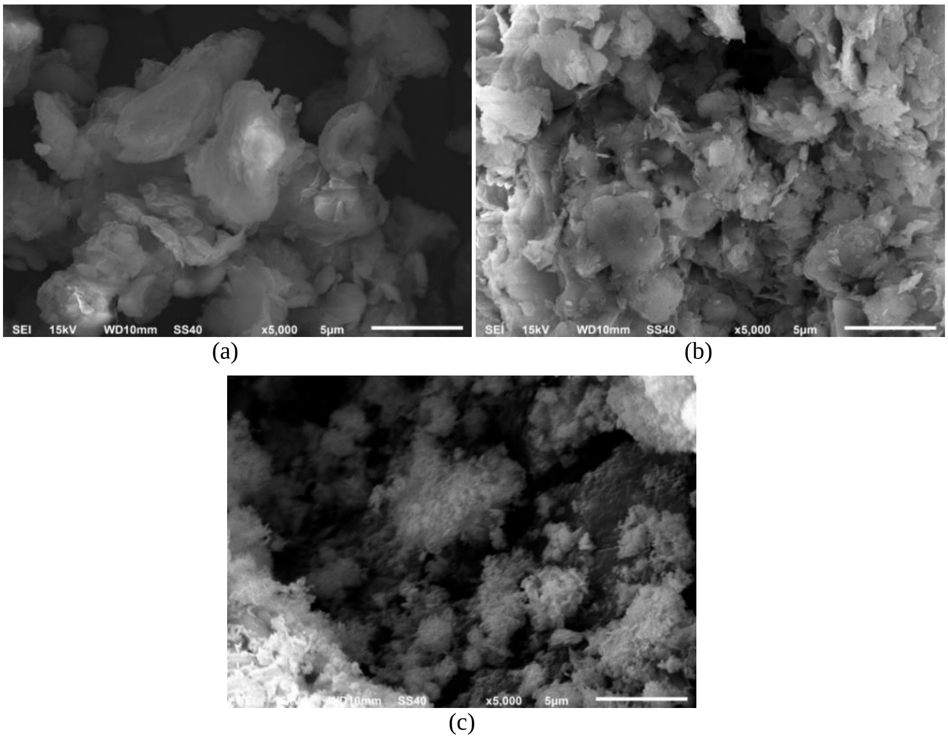


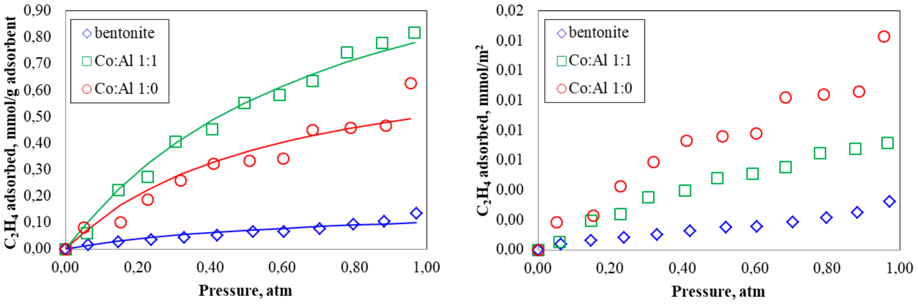
Figure 3 SEM images of (a) natural bentonite, (b) pillared clay Co:Al 1:3, (c) pillared clay Co:Al 1:0.

3.2 Ethylene Adsorption

The adsorption study aimed to evaluate the effectiveness of the adsorbent by analyzing the amount of ethylene adsorbed at various pressures. Figure 4 presents the results of the adsorption test for the natural bentonite and the Co-Al pillared bentonite with a cobalt to aluminum ratio of 1:1 and 1:0.

The adsorption study results for the different materials differed in terms of the equilibrium capacity achieved. The effect of cobalt on adsorption depends on the interaction between cobalt, adsorbent, and adsorbate. As shown in Figure 4(a), the adsorption capacity of the adsorbent increased almost three times for the Co:Al 1:1 material compared to the pristine bentonite (0.8 mmol/g for Co:Al 1:1 at 1 atm). For the Co:Al 1:0 material using only cobalt as pillaring agent there was also an improvement but not as high as for Co:Al 1:1. This may be due to the low specific surface area of Co:Al 1:0 (44 m^2/g). Based on the experimental data shown in Figure 4, an evaluation was performed using equilibrium equations. The parameter values used for the adsorption equilibrium model are presented in Table 3. The best fitted model was the Langmuir model (see fitted line in Figure.

4(a)). The equilibrium constant (*b*) shows the affinity of the materials to ethylene and $C_{\mu s}$ shows the maximum adsorption capacity of the materials to ethylene.



(a) (b)

Figure 4 Ethylene adsorption isotherm curves on various types of bentonite at T = 30 °C. Normalized by mass of adsorbent and fitted by Langmuir model (a) and surface area (b).

Table 3 Equilibrium Parameter Values of Ethylene Adsorption of Various Bentonite Materials at T = 30 °C Evaluated Using Langmuir Model

Parameters	**Material**		
	Natural bentonite	**Co:Al 1:1**	**Co:Al 1:0**
$C_{\mu s}$, mmol/g adsorbent	0.1698	1.3910	0.7899
b, atm^{-1}	1.4520	1.3278	1.7441

Figure 4(b) shows the adsorbed capacity normalized by surface area. The data give an indication of which factors influenced the ethylene uptake. It shows that the pillared bentonite Co:Al 1:1 had an ethylene adsorption capacity normalized by surface area higher than that of the bentonite. This suggests that the most important factor for enhancement of uptake is the surface area and the presence of Co in the material. In contrast, when the amount of Co was high (pillared bentonite Co:Al 1:0), the presence of Co in the material became the most important effect, hence increasing the affinity for ethylene adsorption. This is proven by the high value of the ethylene adsorption capacity normalized by surface area, although the surface area of the material was low.

Some studies describe the ethylene uptake by adsorbents. In this work, the adsorption test result was lower than in other studies based on carbonaceous supports [5,18]. However, it was superior compared to the ethylene uptake result with typical clay minerals, i.e. sepiolite (0.622 mmol/g) [19] and Turkish bentonite (0.572 mmol/g) at 20 °C 37 kPa [20]). Compared to the uptake capacity, it is necessary to optimize the adsorbent manufacture to produce higher capacity adsorbents in ethylene scavengers.

3.3 Proposed Application System

After the adsorption capacity was determined, the Co:Al pillared bentonite was further tested for application. The proposed system is shown in Figure (5). Fruit was put in the storage and a certain amount of adsorbent was placed in the same system. The mass ratio between the adsorbent and the fruit was specified. The day to day condition of the fruit was monitored by color change [5]. The storage shelf life will be the scope of a future study.

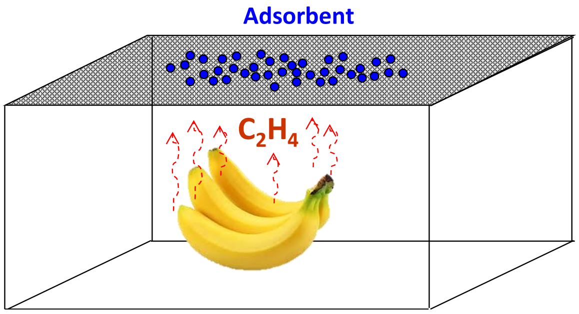


Figure 5 Proposed system for application of adsorbent in storage shelf life using banana fruit as example.

4 Conclusions

Bentonite can be used as a raw material to produce ethylene adsorbent. The modification of bentonite was carried out by pillarization using Co and Al. The characterization of EDX, SEM and pore analysis confirmed that pillared clay was successfully produced. The pillared bentonite showed an increase in specific surface area, with the highest value at 114 m^2/g, featured by Co:Al 1:1. An adsorption capacity of ethylene up to 0.8 mmol/g was achieved, i.e. six times compared to the natural bentonite. It was proved that the effects influencing the adsorption capacity are the pore structure and the presence of Co as active metal. Based on the capability of the adsorbent to adsorb ethylene, further experiments can be performed to study fruit ripening extension using cobalt oxide/pillared clay.

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