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Vegetable waste adsorbers for ethylene gas

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Abstract— **Vegetable wastes occurred annually at the end of production like tomato stem, squash stem, cucumber stem, red perilla stem and bract of corn were regenerated into C2H4 adsorbents. Their wastes were washed with distilled water and then dried for more than 5 days at room temperature. The C2H4 and nitrogen adsorption was examined in their vegetable wastes and the gases adsorption performance was compared with those of zeolite and activated carbon. The results showed that the tomato stem having fine cell walls composed of cellulose fibers had the highest C2H4 adsorption quantity with tested wastes but other wastes showed aggregated cellulose fibers. The C2H4 adsorption volume per unit area of the tomato stem was 0.35 (cm3/m2) and was 2.5 times higher than that of zeolite and the adsorption was obeyed Freundlich model.**

Index Terms— **Vegetable wastes, Ethylene gas, Adsorption, Tomato stem**

I. INTRODUCTION

It is well known that ethylene (C_2H_4) is a gaseous performance in fruits and vegetables naturally produced as ripened chemical [1]. As an aging hormone, C_2H_4 influences the ripening of fruit and vegetable and causes plants to be generally aged, when the plant is exposed in the gas [2], [3]. Nowadays, many of the fruits and vegetables in our neighborhood grocery stores have traveled far away from the produced countries to their consumers. When fruits and vegetables are packaged for a long time, the air in the container circulates and speeds up ripening. As a result, C_2H_4 makes up a significant portion of postharvest losses in developing countries. So in the food industry, the controlling C_2H_4 amount is very important. Generally, It is known that zeolite [4], [5] and activated carbon [6], [7] are porous materials for C_2H_4 adsorbers. This is because that many kinds of micropores in the absorbers provide a wide surface area to adsorb C_2H_4 [8] — [10]. Therefore, the effective way for capturing C_2H_4 for perishable food is physisorption on porous materials.

On the other hand, perishable vegetables and fruits are grown by adsorbing such growth hormone of C_2H_4 [11]. This is because that the phytohormone C_2H_4 inhibits cell expansion in plants, when the gas is present in cellulose microfibers. So, cellulose microfiber in plants seems to include C_2H_4 adsorption sites. However, very limited research was reported [12], [13]. Among them, Walten *et al*. reported growth cotton in effect on C_2H_4 [12]. David *et al.* also reported that tomato showed insensitivity to their growth [13]. This strongly suggests that such plant has C_2H_4 insensitive sites inside plat. Thus, it is interesting to apply such vegetable waste to C_2H_4 adsorber, especially in their inedible parts such as leaves and stems as a recycle green product. Herein, the present paper reports vegetable wastes of tomato stem, squash stem, cucumber stem, red perilla stem and bract of corn for C_2H_4 adsorbents performance.

II. MATERIALS AND EXPERIMENTS

A. *Materials*

Ethanol was purchased from Nacalai Tesque Inc (Tokyo, Japan). Zeolite originally comes from Iizaka Mine was supplied from Nitto Funka Trading Co., Ltd. (Tokyo, Japan). Activated carbon (FP-3) was obtained from JEChem (Osaka, Japan). Tomato stem, squash stem, and bract of corn were made from Fukushima (Japan), cucumber stem was obtained from Aomori (Japan) and the red perilla stem was supplied from Niigata (Japan).

B. *Preparation and characterization of vegetable waste samples*

All vegetable wastes were washed with distilled water and dried more than 5 days at room temperature. The morphology of the vegetable waste was observed by using a scanning electron microscope (SEM, JSM-5300 LV; JEOL, Japan) after gold coating using a quick cool coaster (Sanyu Denshi K.K, Japan). Functional group analysis of the treated vegetable wastes was carried out using Fourier transform infrared (FT-IR) spectroscopy (FT-IR 4100 series, Jasco Corp. Japan) over a frequency range 500-4000 cm^{-1}. Pellets were made from samples with KBr. Moreover, each vegetable waste was cut 5 mm×5 mm for BET surface area measurement and C_2H_4 adsorption experiment.

C. *Gas adsorption experiments for the vegetable wastes*

Following the preparation of vegetable wastes of tomato stem, squash stem, cucumber stem, red perilla stem and bract of corn, BET surface area of their wastes were measured using a Micromeritics Automatic Surface Area and porosimetry Analyzer Tristar II (Shimadzu, Japan). The samples (5 mm× 5 mm) were put in the sample tube and dried by using the micromeritics VacPrep061 (Shimadzu, Japan) at 25℃ for 24 h. Then, the sample tube was launched in the analyzer in the relative pressure range of 1.0×10^{-4} to 9.9×10^{-1} at 77.3 K. Similar experiments for the N_2 adsorption of the vegetable wastes, C_2H_4 adsorption was also measured in the range of 1.0-100k Pa at 273.15 K. These gas adsorption results were compared with those of zeolite and activated carbon. In their experimental results, to compare each value in unit area, the quantity adsorbed of C_2H_4 per unit (Q) was derived from the maximum quantity adsorbed of C_2H_4 (Q_m) and the BET surface area (V) according to following equation, $Q=Q_m/V$.

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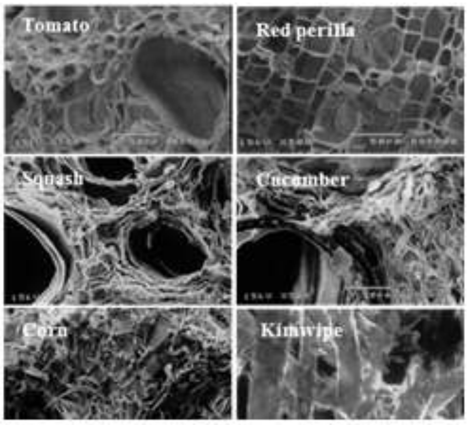

Fig. 1. SEM image of vegetable waste after washing with distilled water and dried for 5 days at room temperature and kimwipe.

D. Analyze for C_2H_4 adsorption in the vegetable waste

Langmuir and Freundlich analyze were followed by their standard methods for analyzing the equilibrium binding parameters for the homogeneous and heterogeneous surface, respectively [14]. In order to investigate the adsorption ability for C_2H_4 in the resultant vegetable wastes, Langmuir (Eq.1) and Freundlich (Eq.2) analyze was taken as follows equations from the result of their C_2H_4 adsorption experiments.

$$\frac{p}{n_a} = \frac{1}{n_m^a K} + (\frac{1}{n_m^a})p \quad (1)$$

$$\ln n^a = \ln a + (\frac{1}{u})\ln P \quad (2)$$

Where a is constant, u is adsorption intensity, p is the adsorbate's partial pressure, and n_a represent the binding capacity of the substrate to vegetable waste.

III. RESULTS AND DISCUSSIONS

A. Characterization of vegetable wastes

Fig. 1 shows the SEM micrographs of the tensile fractured surface of tomato stem, squash stem, cucumber stem, red perilla stem, bract of corn and kimwipe at a magnification of 500×. As seen, the tomato stem, squash stem, cucumber stem and red perilla stem exhibited a fractured surface with many cell walls. Especially tomato stem and red perilla stem had many fine cell walls. However, in the cases of squash stem, cucumber stem and bract of corn, the SEM micrographs exhibited no fine cell walls on the fracture surfaces. The pictures of the squash stem and cucumber stem suggested that fibrous cellulose was strongly aggregated each other. For the comparison, cellulose fiber, kimwipe, was used as a reference sample (Fig. 1, bottom right). In order to examine their porous properties for gas adsorptivity , N_2 adsorption was carried out. Fig. 2(a) shows N_2 adsorption isotherms for their samples. The tomato stem showed the highest BET surface area in vegetable wastes and BET surface area of tomato stem, red perilla stem, squash stem, cucumber stem and bract of corn were 0.76, 0.68, 0.66, 0.54 and 0.43 m^2/g, respectively. As seen in the isotherm of the tomato stem, the type was followed in type II for macro porous structure [15]. In Fig. 2(b), meso pore distribution was calculated by Barrett-Joyner-Halenda method (BJH methods) [16]. The kimwipe, tomato stem and red perilla stem had pore distribution in the range of 150-200 Å. Also the tomato stem and red perilla stem had fine pores in the less than 40 Å regions. This well corresponded to the presence of the many fine cell walls on fractured surface. This also meant that these cells provided a wide surface area. In contrast, the bract of corn and the cucumber stem exhibited the lowest BET surface area in vegetable waste. The BJH pore distribution also suggested less pore volume distribution. The comparison of the BJH results suggested that red perilla stem having fine cell walls had very less pores in less than 50 Å regions, although the stem contacted larger pores having 150-200 Å size.

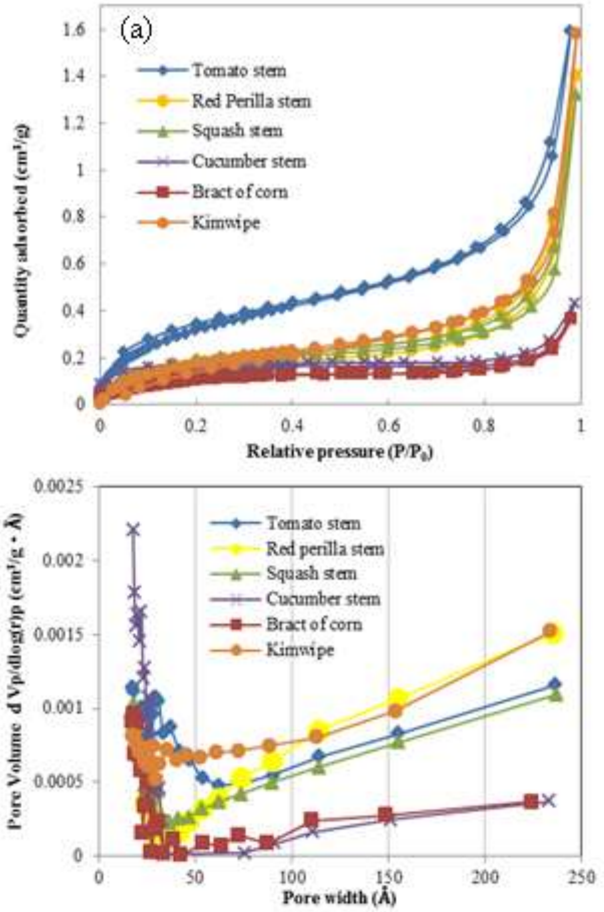

Fig. 2. N_2 isotherm (a) and BJH pore distribution (b) of vegetable wastes and kimwipe.

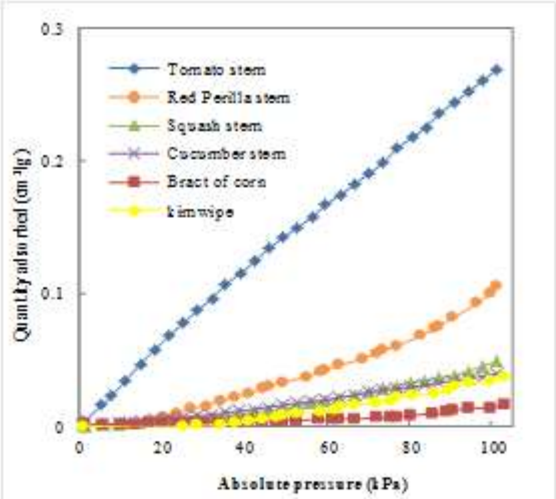

Fig. 3. C_2H_4 isotherm of vegetable wastes and

As seen in Fig. 3, C_2H_4 adsorption experiment was carried out for the vegetable wastes. The C_2H_4 isotherm of the tomato stem had higher adsorption to C_2H_4. The adsorption quantities of tomato stem, red perilla stem, squash stem, bract of corn, cucumber stem and kimwipe were 0.27, 0.10, 0.05, 0.02, 0.04 and 0.04 cm^3/g, respectively at 100k Pa. It was clear that the tomato stem showed the highest C_2H_4 adsorption capacity in the vegetable wastes, meaning the presence of many fine cell walls on fractured surface. However, the red perilla and kimwipe having a similar BET surface area with tomato stem showed one-third and one-seventh lower than C_2H_4 adsorption quantity of the tomato stem, respectively. Therefore, it was indicated that not only physisorption of C_2H_4 occurred on vegetable waste, but also chemisorption occurred especially in tomato stem. The FT-IR spectra of vegetable wastes and lignin, which are comparable with vegetable wastes are shown in Fig.4. All vegetable wastes spectra revealed a broad and intense peak at 3400 cm^{-1} attributed to hydrogen bonded (O-H bond) stretching vibration from the cellulose, whereas a weak absorption peak in the range of 1160-1050 cm^{-1} assigned to C-O-C, C-OH and C-C bonded stretching vibration from the β-(1 → 4')-glycosidic bond. Moreover, they also had a weak absorption peak at 2840 cm^{-1} and 1600-1510 cm^{-1} assigned to C-H bonded stretching from the methoxy group and C=C bonded stretching vibration from the aromatic rings of the lignin suggesting to their presence in vegetable wastes. With these results, it was confirmed that tomato stem, squash stem, cucumber stem, red perilla stem, bract of corn showed the presence of IR peaks of lignin and cellulose. However, kimwipe composing the fibrous structure also exhibited strong O-H bond peak and C-O-C, C-OH and C-C bond at 3400, 1160-1050 cm^{-1}, respectively. These peaks were characterized from cellulose, but there were no peaks at 2840, 1600 and 1510 cm^{-1} for lignin.

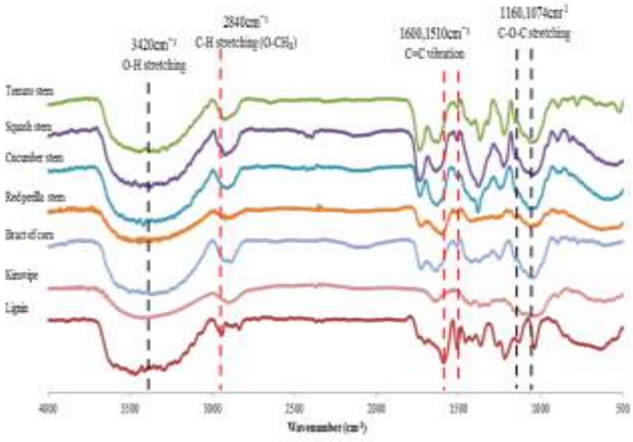

Fig. 4. FT-IR spectra of vegetable wastes, kimwipe and lignin.

B. *Analyses of C_2H_4 adsorption to vegetable wastes*

To know the adsorption behavior, the results of the C_2H_4 adsorption were applied for Langmuir and Freundlich analyzes. The Langmuir plots were obtained by C_2H_4 adsorption experiment for each vegetable waste in Fig. 5(a). From the obtained date, the correlation coefficient (R^2) was calculated of tomato stem, red perilla stem, squash stem, cucumber stalk and bract of corn for -7.52.0.49, -2.23, -10.92, -6.52 and -7.52, respectively. This was indicated that these C_2H_4 adsorption isotherm were not related to unimolecular adsorption on the surface. Fig. 5(b) shows Freundlich plots of the C_2H_4 adsorption. In the case of Feundlich plots, the values of R^2 of tomato stem, red perilla stem, squash stem, cucumber stem and bract of corn were 0.97, 0.99, 0.99, 0.98 and 0.93, respectively. This strongly indicated that the C_2H_4 adsorption isotherm of the vegetable waste obeyed with Freundlich relation, meaning that multi layer adsorption of C_2H_4 was occurred on vegetable wastes. The constant *a* is an approximate indicator of adsorption capacity, while 1/*u* is a function of the strength of adsorption in the adsorption process [17]. The values of constant *a* were 0.0031, 0.0008, 0.0003, 0.0003 and 0.0001 for tomato stem, red perilla stem, squash stem, cucumber stem and bract of corn, respectively.

The adsorptivity of C_2H_4 for the tomato stem was compared with those of zeolite and activated carbon. So, the volume of the C_2H_4 adsorption quantity (Q_a) and BET surface area was converted to the adsorptivity per unit area in the vegetable wastes, zeolite and activated carbon. Fig. 6 shows the quantity of adsorption of C_2H_4 per unit area cm^3/m^2 for each sample. The zeolite and activated carbon had 0.14 and 0.07 cm^3/m^2 in the unit area adsorption to C_2H_4. In contrast, for the case of tomato stem, high adsorption to C_2H_4 occurred with 0.35 cm^3/m^2. This result meant that the tomato stem contained efficient adsorption sites to C_2H_4 it microfibrous cellulose.

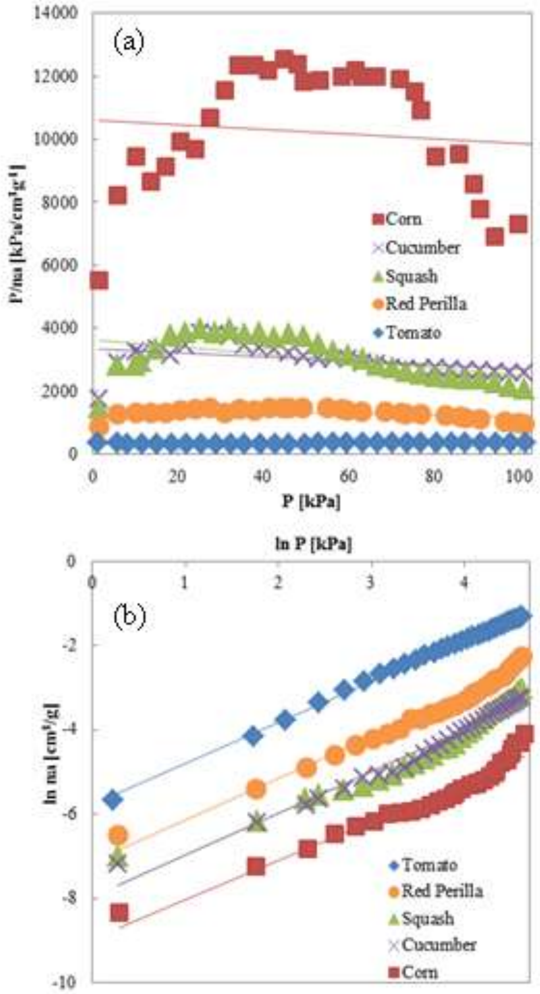

Fig. 5. Langmir plot (a) and Freundlich plot (b) for C_2H_4 in vegetable waste.

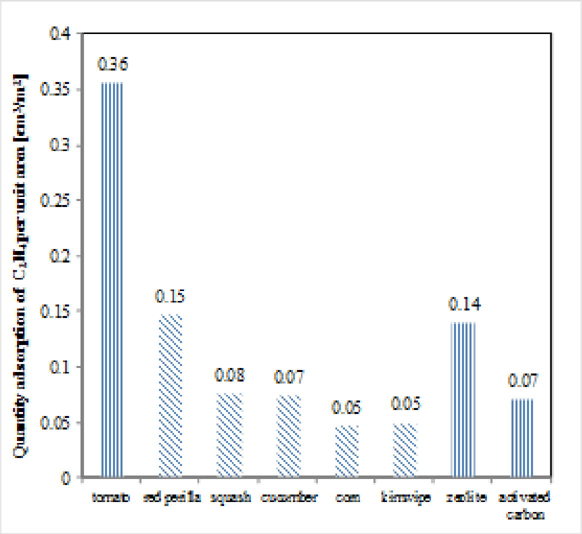

Fig. 6. Quantity adsorption of C_2H_4 gas per unit area of each molecular hosts.

IV. CONCLUSION

In the present paper, high C_2H_4 adsorption was found in tomato stem vegetable waste. The stem morphology developed fine cell walls. The C_2H_4 gas was obeyed by Freindlich plots, meaning that such surface of cellulose microfibrous behaved multi adsorption surface to C_2H_4. So the tomato stem vegetable waste having many fine cell walls had high ability of C_2H_4 adsorber.

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