

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 (C₂H₄) is a gaseous performance in fruits and vegetables naturally produced as ripened chemical [1]. As an aging hormone, C₂H₄ 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, C₂H₄ makes up a significant portion of postharvest losses in developing countries. So in the food industry, the controlling C₂H₄ amount is very important. Generally, It is known that zeolite [4], [5] and activated carbon [6], [7] are porous materials for C₂H₄ adsorbents. This is because that many kinds of micropores in the adsorbents provide a wide surface area to adsorb C₂H₄ [8] – [10]. Therefore, the effective way for capturing C₂H₄ for perishable food is physisorption on porous materials.

On the other hand, perishable vegetables and fruits are grown by adsorbing such growth hormone of C₂H₄ [11]. This is because that the phytohormone C₂H₄ inhibits cell expansion in plants, when the gas is present in cellulose microfibrils. So, cellulose microfibril in plants seems to include C₂H₄ adsorption sites. However, very limited research was reported [12], [13]. Among them, Walten *et al.* reported growth cotton in effect on C₂H₄ [12]. David *et al.* also reported that tomato showed insensitivity to their growth [13]. This strongly suggests that such plant has C₂H₄ insensitive sites inside plant.

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Thus, it is interesting to apply such vegetable waste to C₂H₄ adsorbent, 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 C₂H₄ 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 Funaka 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 coater (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 C₂H₄ 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°C 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 N₂ adsorption of the vegetable wastes, C₂H₄ 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 C₂H₄ per unit (Q) was derived from the maximum quantity adsorbed of C₂H₄ (Q_m) and the BET surface area (V) according to following equation, Q=Q_m/V.

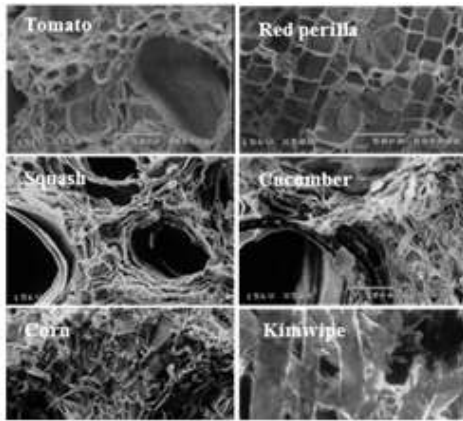


Fig. 1. SEM image of vegetable waste after washing with distilled water and dried for 5 days at room temperature and kimwipe.

D. Analyze for C₂H₄ 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 C₂H₄ in the resultant vegetable wastes, Langmuir (Eq.1) and Freundlich (Eq.2) analyze was taken as follows equations from the result of their C₂H₄ adsorption experiments.

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

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

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, N₂ adsorption was carried out. Fig. 2(a) shows N₂ 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 m²/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.

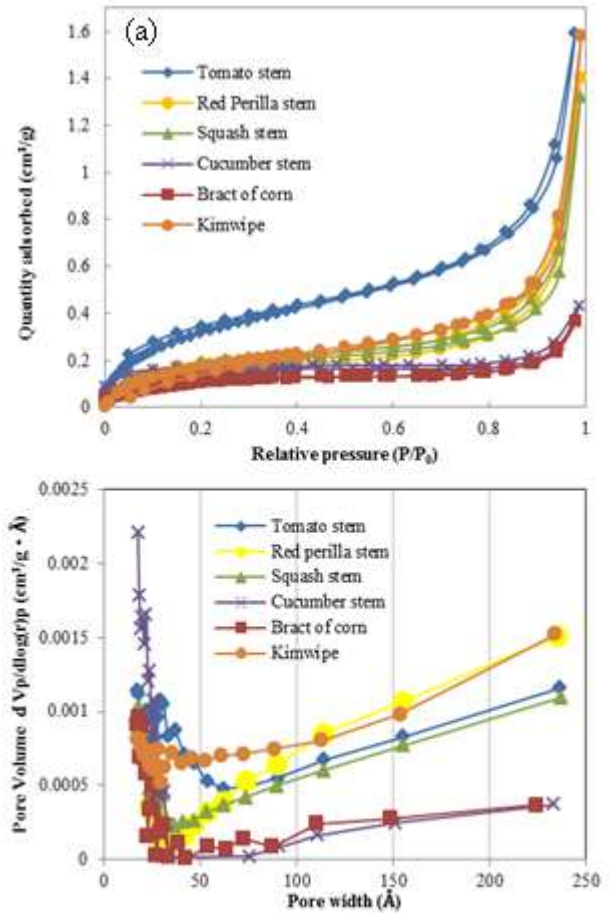


Fig. 2. N₂ isotherm (a) and BJH pore distribution (b) of vegetable wastes and kimwipe.

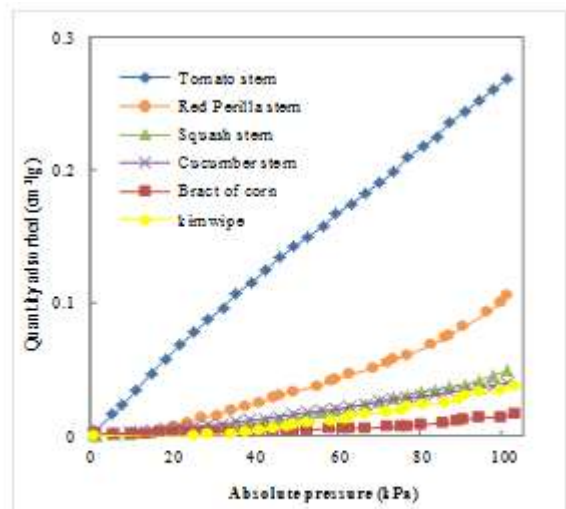


Fig. 3. C₂H₄ isotherm of vegetable wastes and

As seen in Fig. 3, C₂H₄ adsorption experiment was carried out for the vegetable wastes. The C₂H₄ isotherm of the tomato stem had higher adsorption to C₂H₄. 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 cm³/g, respectively at 100k Pa. It was clear that the tomato stem showed the highest C₂H₄ 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 C₂H₄ adsorption quantity of the tomato stem, respectively. Therefore, it was indicated that not only physisorption of C₂H₄ 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.

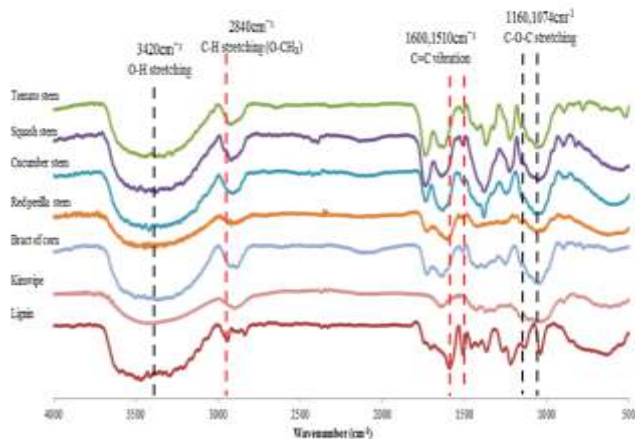


Fig. 4. FT-IR spectra of vegetable wastes, kimwipe and lignin.

B. Analyses of C₂H₄ adsorption to vegetable wastes

To know the adsorption behavior, the results of the C₂H₄ adsorption were applied for Langmuir and Freundlich analyzes. The Langmuir plots were obtained by C₂H₄ adsorption experiment for each vegetable waste in Fig. 5(a). From the obtained date, the correlation coefficient (R²) 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 C₂H₄ adsorption isotherm were not related to unimolecular

adsorption on the surface. Fig. 5(b) shows Freundlich plots of the C₂H₄ adsorption. In the case of Freundlich plots, the values of R² 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 C₂H₄ adsorption isotherm of the vegetable waste obeyed with Freundlich relation, meaning that multi layer adsorption of C₂H₄ was occurred on vegetable wastes. The constant *a* is an approximate indicator of adsorption capacity, while 1/*n* 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 C₂H₄ for the tomato stem was compared with those of zeolite and activated carbon. So, the volume of the C₂H₄ 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 C₂H₄ per unit area cm³/m² for each sample. The zeolite and activated carbon had 0.14 and 0.07 cm³/m² in the unit area adsorption to C₂H₄. In contrast, for the case of tomato stem, high adsorption to C₂H₄ occurred with 0.35 cm³/m². This result meant that the tomato stem contained efficient adsorption sites to C₂H₄ it microfibrus cellulose.

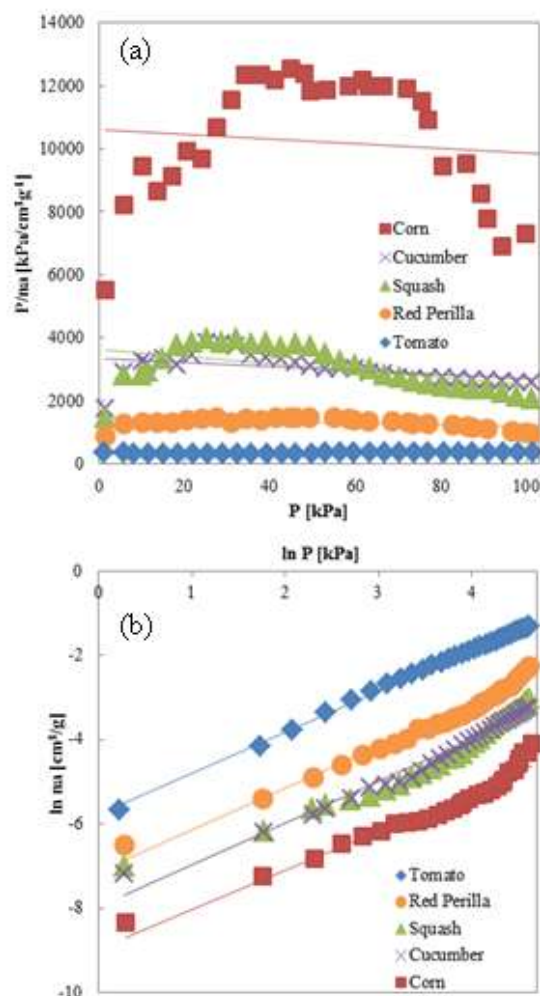


Fig. 5. Langmuir plot (a) and Freundlich plot (b) for C₂H₄ in vegetable waste.

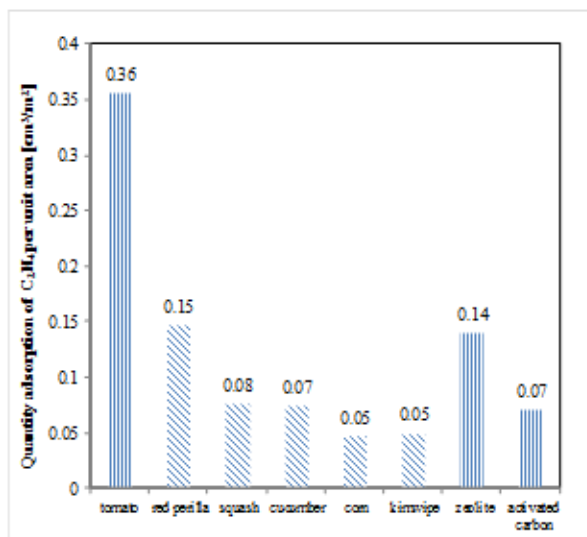


Fig. 6. Quantity adsorption of C₂H₄ gas per unit area of each molecular hosts.

IV. CONCLUSION

In the present paper, high C₂H₄ adsorption was found in tomato stem vegetable waste. The stem morphology developed fine cell walls. The C₂H₄ gas was obeyed by Freundlich plots, meaning that such surface of cellulose microfibrils behaved multi adsorption surface to C₂H₄. So the tomato stem vegetable waste having many fine cell walls had high ability of C₂H₄ adsorber.

REFERENCES

- [1] Z. Lin, S. Zhong, D. Grierson, Recent advances in ethylene research, *Journal of experimental botany*, 60 (2009) 3311-3336.
- [2] A.A. Kader, M.S. Reid, J.F. Thompson, In *Postharvest Technology of Horticultural Crops* (Ed.: A.A. Kader), University of California, Agricultural and Natural Resources, Publication, 3311 (2002) pp. 39 ff.
- [3] D. Robert, *Plant Physiology Third Edition*, Reinhold Book Corp., New York, (1968).
- [4] V.R. Choudhary, S. Mayadevi, Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide on High Silica Pentasil Zeolites and Zeolite-like Materials Using Gas Chromatography Pulse Technique, *Separation Science and Technology*, 28 (1993) 2197-2209.
- [5] G. Calleja, J. Pau, J.A. Calles, Pure and Multicomponent Adsorption Equilibrium of Carbon Dioxide, Ethylene, and Propane on ZSM-5 Zeolites with Different Si/Al Ratios, *Journal of Chemical & Engineering Data*, 43 (1998) 994-1003.
- [6] R. Reich, W.T. Ziegler, K.A. Rogers, Adsorption of Methane, Ethane, and Ethylene Gases and Their Binary and Ternary Mixtures and Carbon Dioxide on Activated Carbon at 212-301 K and Pressures to 35 Atmospheres, *Industrial & engineering chemistry process design and development*, 19 (1980) 336.
- [7] B.U. Choi, D.K. Choi, Y.W. Lee, B.K. Lee, S.H. Kim, Adsorption Equilibria of Methane, Ethane, Ethylene, Nitrogen, and Hydrogen onto Activated Carbon, *Journal of Chemical & Engineering Data*, 48 (2003) 603-607.
- [8] M. Ozdemir, J.D. Floros, Active food packaging technologies, *Critical reviews in food science and nutrition*, 44.3 (2004) 185-193.
- [9] T. Suslow, Performance of zeolite based products in ethylene removal, *Journal of Physical Chemistry*, 101 (1997) 3091-3096.
- [10] A.L. Brody, E.P. Strupinsky, R.L. Kline, *Active packaging for food applications*, CRC press (2001).
- [11] P.B. Stanley, Ethylene in Plant Growth, *Proceedings of the National Academy of Sciences of the United States of America*, 70(2) (1973) 591-597.

- [12] W.H. Walter, E.G. Pires, W.C. Hall, The Effects of a Low Ethylene Concentration on the Growth of Cotton, *Journal of the Air Pollution Control Association*, 11(12) (1961) 549-556.
- [13] G.D. Clark, E.K. Gubrium, J.E. Barrett, T.A. Nell, H.J. Klee, Root Formation in Ethylene-Insensitive Plants, *Plant Physiology*, 121 (1999) 53-59.
- [14] N.D. Hutson, R.T. Yang, Adsorption, *Journal of Colloid and Interface Science*, 3(3) (2000) 189-195.
- [15] Iupac, *Pure Applied Chemistry*, 66 (1994) pp 1739.
- [16] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *Journal of the American Chemical Society*, 73 (1951) 373-380.
- [17] E. Voudrias, F. Fytianos, E. Bosnia, Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials, *Global Nest Journal*, 4(1) (2002) 75-83