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Development of Formaldehyde Adsorption using Modified Activated Carbon – A Review

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ABSTRACT: Gas storage is a technology developed with an adsorptive storage method, in which gases are stored as adsorbed components on the certain adsorbent. Formaldehyde is one of the major indoor gaseous pollutants. Depending on its concentration, formaldehyde may cause minor disorder symptoms to a serious injury. Some of the successful applications of technology for the removal of formaldehyde have been reported. However, this paper presents an overview of several studies on the elimination of formaldehyde that has been done by adsorption method because of its simplicity. The adsorption method does not require high energy and the adsorbent used can be obtained from inexpensive materials. Most researchers used activated carbon as an adsorbent for removal of formaldehyde because of its high adsorption capacity. Activated carbons can be produced from many materials such as coals, woods, or agricultural waste. Some of them were prepared by specific activation methods to improve the surface area. Some researchers also used modified activated carbon by adding specific additive to improve its performance in attracting formaldehyde molecules. Proposed modification methods on activation and additive impregnated carbon are thus discussed in this paper for future development and improvement of formaldehyde adsorption on activated carbon. Specifically, a waste agricultural product is chosen for activated carbon raw material because it is renewable and gives an added value to the materials. The study indicates that the performance of the adsorption of formaldehyde might be improved by using modified activated carbon. Bamboo seems to be the most appropriate raw materials to produce activated carbon combined with applying chemical activation method and addition of metal oxidative catalysts such as Cu or Ag in nano size particles. Bamboo activated carbon can be developed in addition to the capture of formaldehyde as well as the storage of adsorptive hydrogen gas that supports renewable energy.

Keywords: adsorption; bamboo; formaldehyde; modified activated carbon; nano size particles

1. Introduction

Gas storage technology is the method of "adsorptive storage", where the gases are stored in the adsorbed state on the certain "adsorbent". Gas molecules have a density in the adsorbed state which is close to the density of the melting state. Hydrogen storage describes a method for storing hydrogen for later use. Hydrogen storage is used to provide renewable energy sources as a provider of fuel for transportation. Storage by melting method is superior, but this requires a very high cost in terms of equipment and energy required. The method of storing hydrogen is performed in a gas cylinder tube which was filled with an activated carbon. Gas pressure can be flexibly adapted to the gas source. Subsequent adsorption technology is used for the adsorption of formaldehyde which is a toxic gas.

Gaseous formaldehyde is one of the major indoor gaseous pollutants. This volatile organic compound is derived from the paint, decoration materials, polymerizing plate, binder of furniture, fiber carpet **[1, 2]**. Formaldehyde is a reagent for adhesives such as urea formaldehyde and phenol-formaldehyde. Formaldehyde at low concentration can cause

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indisposition of throats at a level of about 0.1 mg/m^3 (0.08 ppm), irritation of eyes and noses at about 1 mg/m^3, difficult breathing at about 10 mg/m^3, injury of respiratory organs at about 40 mg/m^3, and asphyxia above 80 mg/m^3 **[3]**. Even, formaldehyde can also result in lung cancer and eventually death.

Concentration limit allowable that formaldehyde exposed in the air by OSHA Permissible Exposure Limit (PEL) is up to 2 ppm **[4]**. The above limitation is also supported by the Indonesian government rules. In addition, World Health Organization recommended that the guideline for indoor air quality is 0,1mg/m3 for 30 minutes to formaldehyde **[5]**.

Efforts to reduce the content of formaldehyde indoor must be done, given the dangers posed and minimum allowable concentration limits. Several methods have been made to reduce formaldehyde gas phase at room and will be reviewed in this paper.

2. Methods of Removing Indoor Formaldehyde Gas

Efforts to reduce pollutants indoor, especially formaldehyde have been studied including the method of photo-catalyst, plasma, enzymes, and adsorption. There are also combined methods, such as adsorption and catalytic oxidation and adsorption and photo-catalyst. Photo-catalyst oxidation methods for removing formaldehyde gas were done by using nano-structured TiO_2, Ag-TiO_2 and Ce-TiO_2 **[6]** while plasma method were using various discharge plasmas. Liang et al used $NaNO_2$ ferro-electric packed bed dielectric barrier discharge plasma reactor applying high-frequency AC power supply **[7]**. There is also DC Corona discharge plasma that can remove low-concentration of formaldehyde in the air by introduction of MnOx/Al_2O_3 catalyst placed at downstream of the plasma reactor **[8, 9]**. Cycle storage-discharge plasma catalytic process was applied to low-concentration formaldehyde removal from air using a combination of HZSM-5, HZ with Ag, and Cu **[10]**.

Formaldehyde can also be oxidized by alcohol in the present of oxidase enzyme. Alcohol oxidase is isolated from Hansenula polymorpha C-105 mutant overproducing this enzyme in glucose medium. Sigawi et al used a such method for removal and control of airborne formaldehyde **[11]**.

A combination of adsorption and catalytic oxidation method was developed to hybrid catalyst for long lifetime clean removal formaldehyde indoors. This kind of hybrid catalyst was applied by Miyawaki et al using MnOx (functioned as a catalyst) and polyacrylonitril-based nano fiber Activated Carbon (functioned as an adsorbent) **[12]**.

Wide application of photo-catalysis in indoor air purification is limited due to the low formaldehyde level as contaminant of indoor air that can be handled. Lu et al used the nano size TiO_2 particles immobilized on the surface of activated carbon filter which result in four time better removal of formaldehyde than using TiO_2 on a flat glass **[13]**.

3. Adsorption of Formaldehyde Gas on Activated Carbon

Adsorptions of formaldehyde gas on activated carbon have been conducted by several researchers. The activated carbons used varied on their origins and the method of physical or chemical activations. Properties of the activated carbon produced and the performance results in adsorbing formaldehyde gas for several researchers are presented in Table 1. Rong et al. used Rayon-based Activated Carbon Fiber activated by air oxidation at 420^{o}C and heat treatment at 1223K. An oxidation treatment with air, activated carbon shows 260 mL/g formaldehyde adsorption capacity **[14, 15]**. On the heat treatment of activated carbon can adsorbs as much as 336 mL of formaldehyde gas per gram of activated carbon for a continuous intake of 80 ppm of formaldehyde in air. Boonamnuayvitaya et al used activated carbon from coffee residue, impregnated with $ZnCl_2$ and activated in a stream of nitrogen. Based on the isotherm adsorption obtained in their study, maximum formaldehyde adsorbed was 360 mL/g at equilibrium gas concentration of 74216 ppm. Kumagai et al used activated carbon from heat-treated rice husks in the flow of CO_2 **[16]**. Only 0.1 mg/g was adsorbed at 1 ppm of formaldehyde. Pei and Zhang used chemically treated commercial activated carbon (it was not mentioned what kind of treatment they used). The results showed that 0.36 mg/g can be adsorbed at equilibrium concentration of formaldehyde of 2.36 ppm **[17]**. Study on adsorption of gaseous formaldehyde on activated carbon derived from dewatered sewage sludge was conducted by Wen et al. The sewage sludge was carbonized in the flow of N_2 at a temperature 450^{o}C followed by impregnated with $ZnCl_2$ and activated at 750^{o}C. The results showed that formaldehyde adsorption capacity could achieve 74.27 mg/g and 7.62 mg/g **[18]**.

4. Adsorption of Formaldehyde Gas on Modified Activated Carbon

Potential of activated carbon in adsorbing formaldehyde can be increased by adding additives. The additive might be either a material that can generate functional groups to catch formaldehyde molecule on the surface of activated carbon or an oxidative catalyst metal that are also able to increase the attractive force of the activated carbon surface. Results of some studies on characteristics and Formaldehyde Gas adsorption Capacity on modified Activated Carbon are summarized on Table 2.

Table 1
Properties of the activated carbon produced and the performance results in adsorbing formaldehyde gas in some studies

Raw materials for activated carbon	Activation	Surface area (m^2/g)	Process	Formaldehyde gas		Researcher
				Inlet	Amount adsorbed	
Rayon-based activated carbon fiber	Air oxidation at 420°C for 1 h, then treated at 950° for 0.5 h. under N_2 flow	1635	batch	-	583.4 (mL/g)	**[14]**
			Continuous. Flowrate= 500 mL/min.	-	260 (mL/g)	
	At 850°C in steam under N_2 flow, then heat-treatment at 950°C for 0,5 h under N_2 flow	2121	Batch	-	723.6 (mL/g)	**[15]**
			Continuous. Flowrate= 500 mL/min.	80 (mL/g)	336 (mL/g)	
Coffee residue	$ZnCl_2$ (3 part) ; Pyrolisis under N_2 flow for 1 h.	470±12	batch	13767, 30431, 50899, 74216 (ppm)	260, 285, 320, 360 (mL/g)	**[1]**
Rice husk	At 875°C in N_2 flow for 1 h., then at 875°C in a CO_2 flow.	466.9	batch	1.0 (ppm)	0.1 (ppm)	**[16]**
Chemically treated activated carbon	Unkown treatment	970	Continuous	2.36 ±0,1 (ppm)	33.565 (mg/g)	**[17]**
Sewage sludge	Carbonized at 450°C for1.5 h. under N_2 flow, then activated with $ZnCl_2$ (1 part) at 750°C for 120 min.	509.88	Batch	498 ; 0.41 (mg/m^3)	74.27 ; 7.62, (mg/g)	**[18]**

Table 2
Characteristics and Adsorptive Capacity of Formaldehyde Gas on to Activated Carbon

Raw materials for activated carbon	Modification	Surface area, m^2/g	Process	Formadehyde gas		Researcher
				Inlet	Amount adsorbed	
Nutshell	Diaminated with HNO_3 and H_2SO_4 for 24 h, then reduced by Fe powder and HCl for 60 min	950	batch	-	2 (mg/g)	**[19]**
Activated carbon articles (<300 μm)	Mixed with MnO_2 (<10μm) 77%b. Blended with a resin binder to make Board-like air cleaning material		Continuous. Flowrate 500-1000 mL/min	0.25 (ppm)	0.04-0.05 (ppm)	**[20]**
Grafite powder	Modified by 3-aminopropyl-methyldiethoxysilane at 105°C		batch	2.14 (ppm)	76.0, for 4 days ; 36.1, for 6 days ; 91.2, for 8 days ; 66.5, for 13 days (mg/g) ; 0.96 (ppm)	**[2]**
Coal-based Granular activated carbon (commercial)	impregnated with Ag nano particles	641±12	Batch	1000 mg/m^3	100 (mg/g)	**[21]**
			Continuous, Flowrate= 378 mL/min	9±1 (ppm)	1.56 (mg/g)	

Tanada et al used activated carbon from nutshell, diaminated with HNO_3 and H_2SO_4, and impregnated with Fe **[19]**. The capacity of activated carbon obtained on adsorbing formaldehyde gas reached 2 mg/g. Sekine and Nishimura developed a board-like air-cleaning material consisting of activated carbon particles and manganese oxides to remove formaldehyde gas from the air. However, the results were not very good where only 0.05 mg/g can be adsorbed in this material **[20]**. Matsuo et al used graphite powder prepared with 3-aminopropyl-methyldiethoxysilane at 105oC to adsorb formaldehyde. Only little formaldehyde (0.96 ppm) can be adsorbed in their experiments **[2]**. Much better results were obtained by Shin and Song where they used silver nano-particles attached onto the surface of granulated activated carbon (coal based) using the sputtering method. The mass of formaldehyde removed by this combination of adsorption and catalytic oxidation was 2.4 times higher than that by the bare activated carbon at a gas retention time of 0.5 second. The amount adsorbed reached as much as 1.56 mg/g **[21]**.

Table 3
Research Results on Developing Activated Carbon Using Various Agricultural By-Product Materials And Activation Methods

Originally activated carbon	Carbonized	Activation	Activator /sample	Surface area, m²/g	Total Pore volume cm³/g	Researcher
Bamboo	carbonized at 700°C under N_2 flow for 1 h	Activated by KOH at 850 °C for 2 h	1 :1	1896	1.109	**[22]**
Japanese Rice husks	carbonized at 875°C in N_2 flow for 1h	activated at 875 °C in CO_2 flow for 1 h	-	466.7	0.35	**[16]**
Waste bamboo scaffolding	-	Activated by H_3PO_4 firstly at 150ºC and then 600ºC under flowing nitrogen	-	758-1869	0.423-1.044	**[23]**
Vertiver root	Carbonized at 800°C for 1 h, under flow N_2.	Activated in steam under flow N_2 at 80°C for 8 h impregnation H_3PO_4 for 24 h	1:1	1272	1.19	**[24]**
Cotton stalk fiber (China)	KH_2P0_4 4%, (KH_2PO_4+sample) slurry at 105°C, stabilized at 250°C for 30 min, carbonized at 600°C for 30 min, activated at 800°C for 20 min under N_2 flow		1: 60	1287	0.667	**[25]**
Bamboo scaffolding (Hongkong)	(HCl+sample) slurry at 105°C for overnight, Activated at 900°C, 2 h, under flow N_2		4 :1	499	0.258	**[26]**
	(HNO_3+sample) slurry at 105°C for overnight, Activated at 900°C, 2 h, under N_2 flow		4 :1	488	0.288	
	H_2SO_4 slurry at 105°C for overnight, Activated at 900°C, 2 h under N_2 flow		1 :1	553	0.284	
Moso bamboo (Phyllostachys pubescens, Japan	K_2CO_3 slurry at 110°C for 24 h, then 800°C for 1 h under flow N_2		2 :1	2175	1.10	**[27]**
Coconut shell (Indonesia)	KOH at 700°C for 1 h, under N_2 flow.		4 :1	1056	-	**[28]**
Sewage sludge	H_3PO_4 with 800 W under flow N_2 (microwave)		1 :2	290.6	0.168	**[9]**
	$ZnCl_2$ with 800 W under flow N_2 (microwave)		1 :15	377.1	0.243	
Bamboo waste discarded	The dried bamboo/KOH mixture at 800°C under flow N_2 for 3 h		1:2	1532	0.4911	**[29]**
Rice husk (India)	Carbonized on 450°C for 1 h under N_2 flow	$ZnCl_2$, activated 450°C, 2 h	-	180.50	0.027	**[30]**
Argan (*Argania spinosa*) seed shells	carbonized under N_2 flow at 500°C for 3 h,	KOH slurry 60°C then 110°C to dryness, pyrolized under N_2 flow 300°C for 2 h and then at 800°C for 3 h	4:1	2132	2.18	**[31]**

5. Future Development

Efforts on finding more efficient adsorption method for removing formaldehyde gas from air have been continuously conducted by many researchers. Focus of the efforts is to improve the surface area of activated carbon by selecting better raw materials and choosing better activation methods.

Recently, agricultural by-products are the most favorable materials used to make activated carbon, the reasons are that these raw materials are renewable and potentially less expensive to manufacture. Table 3 shows research results on developing activated carbon using various agricultural by-product materials and activation methods. It can be concluded based on the table that bamboo is the most favorable material considering that it can produce large number surface area (550-2100 m^2/g). In addition, chemical activation using KOH also shows better result in term of surface area.

Further improvement to increase the capacity of activated carbon in adsorbing formaldehyde gas can also be done by adding metal oxidative catalyst to increase the attractive force of the activated carbon surface. Among the metal oxidative catalysts, Cu probably is the best choice because it is cheap, no toxic and has highly attractive for formaldehyde molecules or hydrocarbon molecules, in general. Addition of Ag nano particles on the surface of activated carbon, as done Shin and Song, however, is also a good alternative. It will not only increase the attractiveness of the activated carbon surface but also increase the surface area of the carbon, therefore increasing the capacity of the gas formaldehyde adsorption. Even though Ag is less reactive oxidation catalyst than Cu, but the size of a silver metal in nano size will create more adsorption sites that can improve the performance of activated carbon adsorption.

6. Conclusion

The efforts to improve the performance of the adsorption of formaldehyde can be done by using modified activated carbon. Bamboo seems to be the most appropriate raw materials to produce activated carbon combined with applying KOH chemical activation method. Furthermore, addition of metal oxidative catalysts such as Cu or Ag in nano size particles will enhance the capacity of activated carbon in adsorbing formaldehyde gas. Further development of an active carbon can be used to adsorb and store hydrogen gas for hydrogen renewable energy sources.

References

[1] Boonamnuayvitaya V, Sae-ung S, Tathapanichakoon W (2005) Preparation of Activated Carbon from Coffee residue for the Adsorption of Formaldehyde. Separation and Purification Technology Vol: 42: 159-168.

[2] Matsuo Y, Nishino Y, Fukutsuka T, Sugie Y (2008) Removal of Formaldehyde from Gas Phase by Silylated Graphite Oxide Containing Amino Group. Carbon Vol. 46: 1159-74.

[3] Shi QW, Jia DY, Geng SB (2005) Prime Criminal of Indoor Air Pollution-Formaldehyde. China Journal Contamination Control Air Condition Technology Vol. 2: 38-44.

[4] MSDS Material Data Safety Sheet (2000) Formaldehyde, Canada: Mallinckrote Baker, Inc

[5] WHO (2010) World Health Organization Guidelines for Indoor Air Quality: Selected Pollutants, World Health Organization Regional Office of Europe.

[6] Liang W, Li J, & Jin Y (2012) Photo-catalytic Degradation of Gaseous Formaldehyde by TiO_2/UV, Ag/TiO_2/UV and Ce/TiO_2/UV. Building and Environment, 51: 345-350.

[7] Liang W, Li J, Li J-X, Zhu T, & Jin Y-Q (2010). Formaldehyde Removal from Gas Streams by Means of $NaNO_2$ Dielectric Barrier Discharge Plasma. Journal of Hazardous Materials, 175: 1090-95.

[8] Fan X, Zhu T, Sun Y, & Yan X (2011) The Roles of Various Plasma Species in The Plasma and Plasma-Catalytic Removal of low-concentration Formaldehyde in Air. Journal of Hazardous Materials, 196: 380-385.

[9] Wang X, Liang X, Wang Y, Wang X, Liu M, Yin D, Xia S, Zhao J, & Zhang Y (2011) Adsorption of Copper (II) onto Activated Carbons from Sewage Sludge by Microwave-induced Phosphoric Acid and Zinc Chloride Activation. Desalination, 278: 231–237.

[10] Zhao D-Z, Li X-S, Shi C, Fan H-Y, & Zhu A-M (2011) Low-Concentration Formaldehyde Removal from Air Using A Cycled Storage-discharge (CSD) Plasma Catalytic Process. Chemical Engineering Science, 66: 3922-29.

[11] Sigawi S, Smutok O, Demkiv O, Zakalska O, Gayda G, Nitzan Y, Nisnevitch M, & Gonchar M (2011) Immobilized Formaldehyde-Metabolizing Enzymes from Hansenula polymorpha for Removal and Control of Airborne Formaldehyde. Journal of Biotechnology, 153: 138-144.

[12] Miyawaki J, Lee G-H, Yeh J, Shiratori N, Shimohara T, Mochida I, & Yoon S-H (2011) Development of Carbon-Supported Hybrid Catalyst for Clean Removal of Formaldehyde Indoors. Catalysis Today, 185: 278-283.

[13] Lu Y, Wang D, Ma C, & Yang H (2010) The Effect of Activated Carbon Adsorption on The Photocatalytic Removal of Formaldehyde. Building and Environment, 45: 615-621.

[14] Rong H, Ryu Z, Zheng J, & Zhang Y (2002) Effect of Air Oxidation of Rayon-based activated Carbon Fibers on Adsorption Behavior for Formaldehyde. Carbon, 40: 2291-300.

[15] Rong H, Ryu Z, Zheng J, & Zhang Y (2003) Influence of Heat Treatment of Rayon-based activated Carbon Fibers on The Adsorption of Formaldehyde. Journal of Colloid and Interface, 261: 207-212.

[16] Kumagai S, Sasaki K, Shimizu Y, & Takeda K (2008) Formaldehyde and Acetaldehyde Adsorption Properties of Heat-Treated Rice Husk. Separation and Purification Technology, 61: 398-403.

[17] Pei J, & Zhang JS (2011) On Performance and Mechanisms of Formaldehyde Removal by Chemi-sorbents. Chemical Engineering Journal, 167: 59-66.

[18] Wen Q, Li C, Cai Z, Zhang W, Gao H, Chen L, Zeng G, Shu X, & Zhao Y (2011) Study on Activated Carbon Derived from Sewage Sludge for Adsorption of Gaseous Formaldehyde. Bioresource Technology, 102: 942-947.

[19] Tanada S, Kawasaki N, Nakamura T, Araki M, & Isomura M (1999) Removal of Formaldehyde by Activated Carbons Containing Amino Groups. Journal of Colloid and Interface Science, 214: 106-108.

[20] Sekine Y, & Nishimura A (2001) Removal Formaldehyde from Indoor Air by Passive Type Air-cleaning Materials. Atmospheric Environment, 35: 2001-7.

[21] Shin SK & Song JH (2011) Modeling and Simulations of The Removal of Formaldehyde Using Silver Nano-particles Attached to Granular Activated Carbon. Journal of Hazardous Materials, 194: 385–392.

[22] Hameed BH, Din ATM, & Ahmad AL (2007) Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics

and Equilibrium Studies. Journal of Hazardous Materials, 141: 819–825.

[23] Chan LS, Cheung WH, & McKay G (2008) Adsorption of Acid Dyes by Bamboo Derived Activated Carbon. Desalination, 218: 304–312.

[24] Altenor S, Carene B, Emmanuel E, Lambert J, Ehrhardt J-J, & Gaspard S, (2009) Adsorption Studies of Methylene Blue and Phenol onto Vetiver Roots Activated Carbon Prepared by Chemical Activation. Journal of Hazardous Materials, 165: 1029–39.

[25] Li K, Zheng Z, Huang X, Zhao G, Feng, J, & Zhang J (2009) Equilibrium, Kinetic,and Thermodynamic Studies on The Adsorption of 2- Nitroaniline onto Activated Carbon Prepared from Cotton Stalk Fibre. Journal of Hazardous Materials, 166: 213-220.

[26] Mui ELK., Cheung WH, Valix M, & McKay G (2010) Activated carbons from bamboo scaffolding using acid activation. Separation and Purification Technology, 74: 213–218.

[27] Horikawa T, Kitakaze Y, Sekida T, Hayashi J, & Katoh M (2010) Characteristics and humidity control capacity of activated carbon from bamboo. Bioresource Technology, 101: 3964–69.

[28] Sudibandriyo M (2011) Production of Super Activated Carbon from Coal and Coconut Shell using Chemical Activation. International Journal of Chemical Engineering Research, 3: 81-88.

[29] Hirunpraditkoon S, Tunthong N, Ruangchai A, & Nuithitikul K (2011) Adsorption Capacities of Activated Carbons Prepared from Bambu by KOH Activation. World Academy of Science. Engineering and Technology, 78: 711-715.

[30] Sharma YC (2011) Adsorption Characteristics of a Low-Cost Activated Carbon for the Reclamation of Colored Effluents Containing Malachite Green. Journal Chemical Engineering Data, 56: 478–484.

[31] Elmouwahidi A, Zapata-Benabithe Z, Carrasco-Marín F, & Moreno-Castilla C, (2012) Activated Carbons from KOH-Activation of Argan (Argania spinosa) Seed Shells as Supercapacitor Electrodes. Bioresource Technology, 111: 185-190.