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Thermodynamics of Formaldehyde Removal by Adsorption onto Nanosilver Loaded Bamboo-Based Activated Carbon

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Abstract. The performance of nanosilver loaded bamboo-based activated carbon as an adsorbent used for the adsorptive removal of formaldehyde in the air. The size porous of the active carbon is predominantly on the size of mesoporous and microporous. Adsorption tests have been evaluated in laboratory scale fixed-bed column, at different temperatures and initial formaldehyde concentration. In order to investigate is both equilibrium and thermodynamic aspects. The experimental data was fitted with Langmuir model and fit well with the adsorption capacity of 91-110 mg/g. The increase in temperature reduces the adsorption capacity. The thermodynamic parameters show that the values of ΔG^o obtained to confirm the feasibility of activated carbon effective sorbents of formaldehyde. The formaldehyde adsorption process is exothermic and adsorbent has a good affinity to formaldehyde.

Introduction

Formaldehyde is one of gas pollutant cause irritation of the skin, eyes, nose, and throat such as. High levels of exposure may cause some types of nasopharyngeal cancer [1] and it is related to know more about its removal. Formaldehyde is a human carcinogen that is also used in permanent press fabrics and in paper products. The formaldehyde in indoor air is often found in nail salons and mainly emitted from interior decoration materials, in paints, glues, lacquers, plywood, particleboard, and adhesives for wallpapers, commonly used in construction and furnishing. In fact, it is required to remove formaldehyde and other dangerous chemicals. The low concentration of formaldehyde determines the low thermodynamic driving force available for capturing of formaldehyde. Therefore, to achieve a high level eliminate of formaldehyde, a large gas volume to be treated with high equipment and operational costs. These issues are a drive to the development of sophisticated cost effective formaldehyde capture process.

Adsorption seems to be a very promising technology and is widely used for gas handling for good removal efficiency, great flexibility and armpits presenting byproducts. Some are used as an adsorbent in accordance with kind of adsorbate. Activated carbon is generally cheaper when compared to zeolite, mesoporous silica, activated carbon and metal organic framework, exhibiting a wide range of pore sizes and surface properties, the result showed that activated carbon has higher adsorption capacity [2]. Synthesis of activated carbon powder from bamboo with silver nanoparticles additive used as pollutant adsorbents. Nanosilver attached to the activated carbon is aimed at improving the ability of adsorption of formaldehyde as well as anti-microbial [3].

In the present work, a bamboo-based activated carbon, obtained from a char bamboo was activated by potassium hydroxide, was produced for formaldehyde adsorption application. Adsorbent synthesis and characterization procedure aim to improve the ability of activated carbon applications. The adsorption test consist of formaldehyde in the air do the different operating conditions on a laboratory scale using a fixed-bed column system. The kinetic and thermodynamic study of adsorption of formaldehyde investigated to determine the real potential of the production of activated carbon modified by nanosilver to capture formaldehyde from the air.

The activated carbon (bamboo) used was obtained from a local area. The bamboo pieces were burnt in the furnace at a temperature of 350 °C for an hour. The charcoal of bamboo produced was withdrawn from the furnace and sieved. The activated carbon had conducted as Rengga's method [4]. Furthermore nanosilver synthesized was conducted with reduction process. As much 4 mL of 0.1 M $AgNO_3$ added to 1 L of a solution with 0.15 wt% of the soluble starch. The mixture vigorously stirred for 1 h under atmosphere. The solution adjusted to 8.0 at final pH by adding NaOH solution. The mixture was maintained at 50^o C until a solution became yellow. The next step, nanosilver in solution was mixed with 108 g of activated carbon under magnetic stirring, resulting in the deposition of about 4 wt% of nanosilver on activated carbon. The activated carbon modified was filtered then washed with distilled water then dried at 105^{o}C until its get a constant weight.

Adsorbent bamboo-based activated carbon with addition nanosilver was used for the adsorption experiments of formaldehyde, which were performed in fixed beds (glass tube ID, 10 mm; length, 50 mm). Fixed beds filled with either the activated with a bed height of 3 cm was also designed. A schematic diagram, Fig. 1, shows the equipment used for the adsorption of gaseous formaldehyde in air. Research-grade air flowed through a flowmeter and passed through formaldehyde solution to generate formaldehyde in the air. Another stream of air flowed through the second flowmeter. Adjustment of the air flow was used to obtain a concentration of formaldehyde desired in the mixing chamber. The streams that contained formaldehyde and pure air met in the fixed-bed filled with NaOH to adsorb all of the water in the streams.

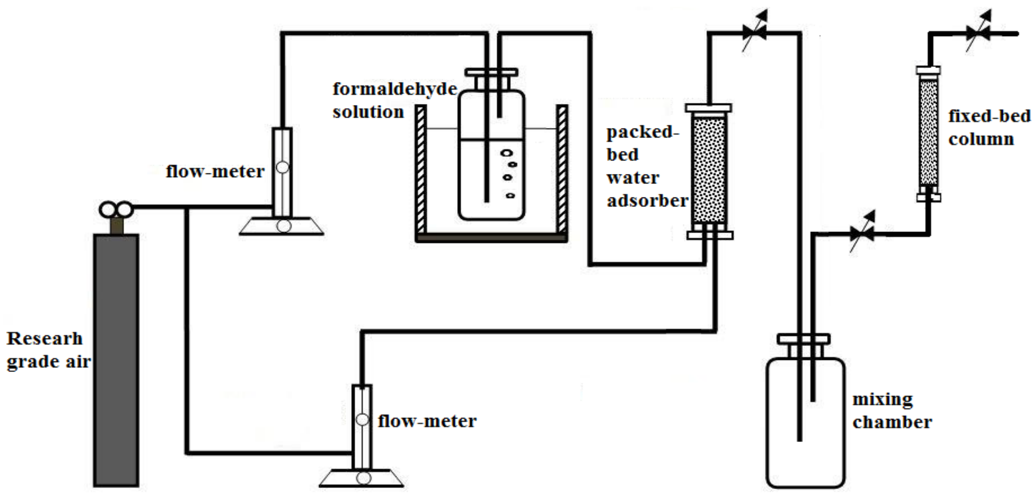

Fig. 1. Schematic diagram of adsorption formaldehyde in a fixed bed.

The inlet and outlet concentrations of formaldehyde were collected using a 0.5 mL gas-tight syringe. Furthermore, the sample was analyzed immediately by using gas chromatography equipped with a flame ionization detector (GC/FID, Shimadzu GC-2014).

The Adsorption Isotherms Different Temperatures

The adsorption isotherms of formaldehyde at different temperatures on activated carbon samples were fitted to standard Langmuir isotherm models. The Langmuir isotherm equation can be represented by Eq. 1. This qe is the amount of formaldehyde adsorbed at the formaldehyde concentration equilibrium and qm is the amount of formaldehyde adsorbed with monolayer coverage. The values qm and Langmuir constant $\boldsymbol{kC}$, calculated from the formaldehyde adsorption isotherms.

$$qe = \frac{qm.kC}{1+kC} \tag{1}$$

The Adsorption Thermodynamics

The thermodynamic parameters that must be considered to determine the process are changes in standard enthalpy (ΔH^o), standard entropy (ΔS^o) and standard free energy (ΔG^o) due to a transfer of unit mole of solute from solution onto the solid–liquid interface. The value of ΔH^o and ΔS^o were computed using the following Eq. 2. Where R (8.314 J/mol K) is the universal gas constant, T (K is the absolute solution temperature and K_d is the distribution coefficient. where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration.

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}; K_d = \frac{C_{Ae}}{C_e}; \quad \Delta G^o = -RT\ln K_d \tag{2}$$

Textural Characterization of Prepared Activated Carbon Modified Nanosilver

Bamboo based activated carbon modified by nanosilver has BET surface area of the prepared to be 1019 m^2/g, with a total pore volume of 0.083 cm^3/g. Fig. 2 shows that the carbon structure of the activated carbon has a pore size of 21-51 nm. The size porous of the active carbon is predominantly on the size of mesoporous and microporous.

Figure 3 shows that the nanosilver (small spheres white image) is seen attached to the activated carbon. Nanosilver is spring ball shape with the distribution between 4-15 nm and most sizes of 5 nm with an average diameter of about 9.2 nm. The size of nanoparticles has a high antimicrobial ability as well as had been reported by Ivask *et al*. [5]. Nanosilver size distribution is more uniform and smaller in size when compared with those reported by Ag nanoparticles Ghaedi *et al.* reach of 15-80 nm [6].

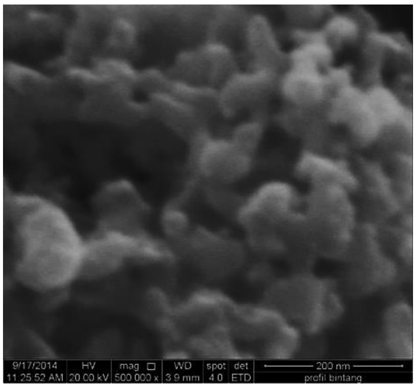

Fig. 2. Morphology FESEM of Bamboo-based Activated Carbon with Addition Nanosilver.

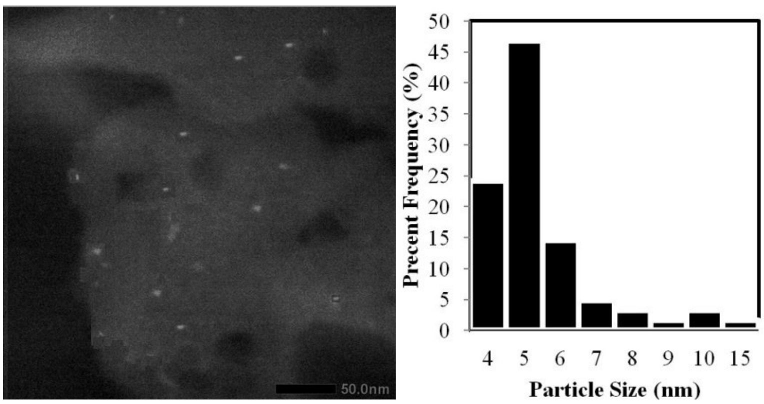

Fig. 3. TEM Image for Bamboo-based Activated Carbon with Addition Nanosilver and Size Distribution of Nanosilver.

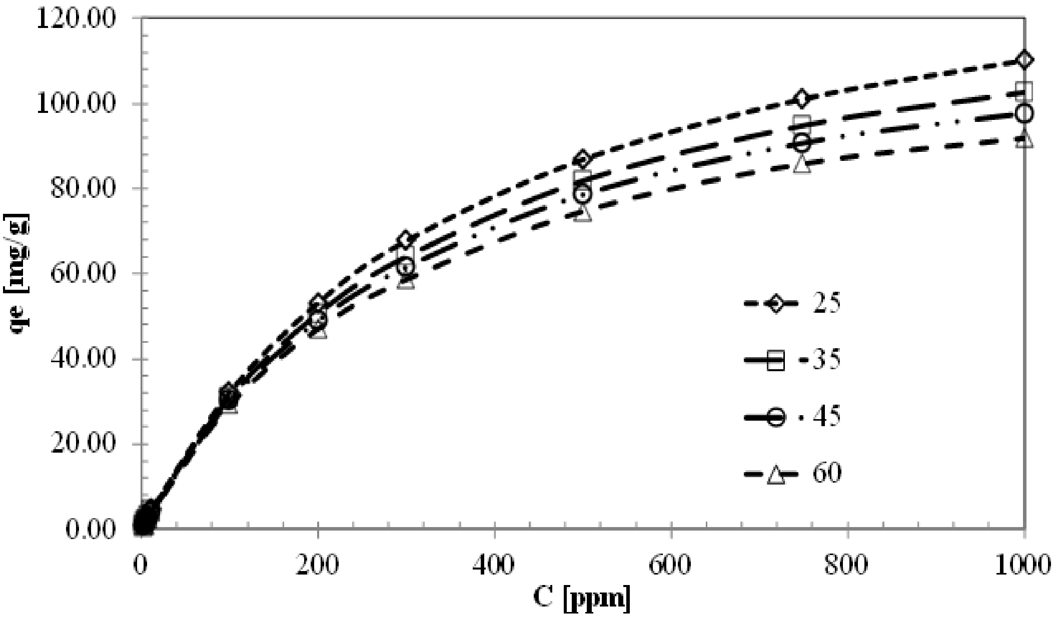

Fig. 4. Formaldehyde Adsorption at Different Temperature on Activated Carbon.

Table 1. Langmuir and Thermodynamic Parameters of Adsorption Formaldehyde.

Temperature	25°C	35°C	45°C	60°C
Langmuir constants qm [mg/g]	110.05	102.55	97.80	91.83
Langmuir constants K [1/ppm]	3745	3403	3180	2923
R^2	0.979	0.989	0.969	0.991
ΔG^o[J/mol]	-20.386	-20.825	-21.404	-22.094
ΔH^o [J/mol]	-675.84			
ΔS^o [J/mol.K]	49.51			

Adsorption isotherm of formaldehyde with activated carbon have been studied previously by Rengga [7], while the adsorption at different temperature is shown in Fig. 4 The adsorption capacity was found out to be 91 to 110 mg/g formaldehyde by activated carbon as adsorbent, while uptake capacity for formaldehyde was 3.41 mg/g using kaolin and 5.03 mg/g using bentonite. The activated carbon is a greater adsorption capacity than kaolin and bentonite [8].

It can also be concluded that by increasing the pressure there is a corresponding increase in formaldehyde adsorption while the adsorption decreases with increase in temperature which according to Dinker and Kukarni [9]. This is due to the fact that increase in the temperature excited the internal energy of the adsorbent which tends to release the formaldehyde present on the adsorbent.

The detail thermodynamic parameters for formaldehyde adsorption on bamboo-based activated carbon with addition nanosilver are given in Table 1. The temperature effect on the adsorption of formaldehyde was studied at 25°C, 35°C, 45°C and 60°C. The negatives values in $\Delta G°$confirm that feasibility of the process and the spontaneous nature of the adsorption process. The negative values of $\Delta H°$ indicated that the adsorption reaction is exothermic for the adsorbent used while the positive value of $\Delta S°$ indicated reflects the affinity of the adsorbents with formaldehyde enthalpy comparison to the process of adsorption of formaldehyde gas, CO_2 and CH_4 by activated carbon which is equally exothermic with $\Delta H°$ of CO_2 highest value and followed CH_4, the lowest was formaldehyde [10].

Conclusion

In this study, a fixed bed adsorption process was employed to determine the adsorption capacity of bamboo-based activated carbon with addition nanosilver. The results showed that the activated carbon have relatively potentially considerable for formaldehyde adsorption. The experimental data was fitted well with Langmuir model. The result also shows that formaldehyde adsorption capacity reduces in an increase in temperature. The thermodynamics parameter shows that the formaldehyde adsorption process is exothermic.

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References

[1] G.M. Marsh, A.O. Youk, J.M. Buchanich, S. Erdal, N.A. Esmen: Regul. Toxico. Pharm. 48 (2007), p. 308.

[2] J-P Bellat, I. Bezverkhy, G. Weber, S. Royer, R. Averlant, J-M Giraudon, J-F. Lamonier: J. Hazard. Mater. 300 (2015), p. 711.

[3] K. Szczepanowics, J. Stefanska, R.P. Socha, P. Warszynski: Psysicochem. Probl. Miner. Process 45, (2010), p. 85.

[4] W.D.P. Rengga, M. Sudibandriyo and M. Nasikin: IJCEA Vol. 4,(2013), p. 334.

[5] A. Ivask, A. ElBadawy, C. Kaweeteerawat, D. Boren, H. Fischer, Z. Ji, C.H. Chang, R. Liu, T. Tolaymat, D. Telesca, J.I. Zink, Y. Cohen, P.A. Holden, H.A. Godwin. ACS Nano 8 (1), (2014), p. 374.

[6] M. Ghaedi, M.N. Biyareh, S.N. Kokhdan, S.Shamsaldini, R. Sahraei, A. Daneshfar and S.Shahriyar: Mater. Sci. Eng ,Vol. C32 (2012), p. 725.

[7] W.D.P. Rengga, M. Sudibandriyo, M. Nasikin. MATEC Web of Conferences 59, (2016), 04004 .

[8] M. Salman, M. Athar, U. Shafique, R. Rehman, S. Ameer, S.Z. Ali, M. Azeem: Turkish J. Eng. Env. Sci. 36 (2012), p. 263.

[9] M.K. Dinker and P.S. Kulkarni: New J. Chem. 39, (2015), p. 3687.

[10] T.T. Trinh, T.S. van Erp, D. Bedeaux, S. Kjelstrup, C.A. Grande: Phys. Chem. Chem. Phys. (2015) online version.