

Modeling and simulations of the removal of formaldehyde using silver nano-particles attached to granular activated carbon

SeungKyu Shin, JiHyeon Song*

Department of Civil and Environmental Engineering, Sejong University, Gunja-Dong 98, Gwangjin-Gu, Seoul, Republic of Korea

ARTICLE INFO

Article history:

Received 12 April 2011

Received in revised form 20 July 2011

Accepted 1 August 2011

Available online 7 August 2011

Keywords:

Silver nano-particles

Catalytic oxidation

Activated carbon

Formaldehyde

Homogeneous surface diffusion model

ABSTRACT

A combined reaction, consisting of granular activated carbon (GAC) adsorption and catalytic oxidation, has been proposed to improve the removal efficiencies of formaldehyde, one of the major indoor air pollutants. In this study, silver nano-particles attached onto the surface of GAC (Ag-GAC) using the sputtering method were evaluated for the simultaneous catalytic oxidation and adsorption of formaldehyde. The evolution of CO₂ from the silver nano-particles indicated that formaldehyde was catalytically oxidized to its final product, with the oxidation kinetics expressed as pseudo-first order. In addition, a packed column test showed that the mass of formaldehyde removed by the Ag-GAC was 2.4 times higher than that by the virgin GAC at a gas retention time of 0.5 s. However, a BET analysis showed that the available surface area and micro-pore volume of the Ag-GAC were substantially decreased due to the deposition of the silver nano-particles. To simulate the performance of the Ag-GAC, the homogeneous surface diffusion model (HSDM), developed for the prediction of the GAC column adsorption, was modified to incorporate the catalytic oxidation taking place on the Ag-GAC surface. The modified HSDM demonstrated that numerical simulations were consistent with the experimental data collected from the Ag-GAC column tests. The model predictions implied that the silver nano-particles deposited on the GAC reduced the adsorptive capacity due to decreasing the available surface for the diffusion of formaldehyde into the GAC, but the overall mass of formaldehyde removed by the Ag-GAC was increased due to catalytic oxidation as a function of the ratio of the surface coverage by the nano-particles.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Indoor air quality problems, such as sick building syndrome, have become of serious environmental concern [1]. Recently, guidelines and regulations on indoor air quality have been legislated for public offices and buildings in many countries. Formaldehyde is one of the most common pollutants present in indoor air, as it is emitted from various building materials including furniture and household products. Formaldehyde causes sneezing and coughing, and leads to acute poisoning, dermal allergies and allergic asthma; therefore, the World Health Organization has recommended a short-term guideline of 0.1 mg/m³ for a 30 min exposure to prevent sensory irritation in the general population [2]. As a result, appropriate air treatment technologies need to be applied for the effective control of formaldehyde in indoor air.

Adsorption using granular activated carbon (GAC) is one of the most common methods for the removal of formaldehyde at low concentrations in indoor air. Although GAC is an excellent absorbent for most of organic compounds, formaldehyde, a

hydrophilic and polar chemical, is generally difficult to adsorb onto GAC. Moreover, even after adsorption by GAC, formaldehyde can be desorbed to the air phase in cases of competitive conditions with other chemicals having higher adsorbing potentials. To enhance the adsorptive capacity of activated carbon for formaldehyde, activated carbon fibers and nano-sized materials have been developed by several researchers [3,4]. Surface modification using amino groups has also been applied to improve the adsorptive capacity of GAC for formaldehyde [5]. Another approach for increasing the removal efficiency of formaldehyde is to simultaneously apply catalytic oxidation with GAC adsorption. Photo-catalysts [6] or silver catalysts [7] have been shown to be effective methods when used in series with activated carbon, but the combined process still needs to be improved to achieve high and reliable formaldehyde removals.

Many studies using silver have been conducted in the areas of biological science and environmental engineering, as metallic silver (Ag⁰) or silver ion (Ag⁺) has long been known to have antibacterial ability without harmful effects on the human body [8]. Silver is also capable of catalytically oxidizing organic compounds on its metal surface. Even though the oxidation potential of silver is relatively lower than other catalysts such as titanium dioxide, it possesses high applicability for use of controlling indoor air due to its non-toxic feature and economical advantages over other pre-

* Corresponding author. Tel.: +82 2 3408 3819; fax: +82 2 3408 4332.
E-mail address: songjh@sejong.ac.kr (J. Song).

cious metals. Silver nano-particles induce more effective catalytic oxidation than bulk-sized metals due to their large specific surface area [9]. The catalytic oxidation of silver nano-particles is strongly associated with the adsorption and reaction of molecular oxygen in air. At room temperature, the molecular oxygen on the surface of silver nano-particles decomposes into oxygen atoms or ions, which have a high oxidation capability [10,11]. According to a mechanism proposed for the oxidation reaction by silver nano-particles, the atoms or molecules of oxygen adsorbed onto the surface of silver particles might provide or accept electrons leading to the formation of reactive oxygen, which then oxidizes the organic compound in air [12–14]. When the Ag nano-particles in the state of Ag⁰ are self-oxidized into Ag⁺ in the procedure of inducing repetitive catalytic oxidation, the oxidation performance may decrease as the catalytic activity decreases. However, the catalyst can be reactivated by reducing Ag⁺ into Ag⁰ by a physicochemical method [15,16]. However, for the management of indoor air quality control, a simple reactivation method should be suggested and evaluated.

The homogeneous surface diffusion model (HSDM) was developed and has been widely used for the numerical analysis of the packed-bed GAC column in either the water or gas phase [17]. For the operation of the GAC column, the HSDM takes into accounts both the advection of pollutants in the bulk phase and the diffusion of pollutants into the solid, GAC phase. The homogeneous diffusion into GAC particles is governed by the surface diffusion coefficient (D_s), which is a characteristic parameter of a target chemical. The HSDM utilizes the Freundlich isotherm for the adsorption onto the surface and inside of GAC particles. The HSDM simulation provides reliable predictions for the performance of the column adsorption under ideal conditions. Since the HSDM can only consider the adsorption for the removal of the target compound, it is impossible to simulate other chemical reactions occurring simultaneously with the GAC adsorption. A modified model is, therefore, required to predict the performance of combined reactions, e.g. catalytic oxidation and adsorption.

In this study, silver nano-particles were attached onto the surface of GAC (Ag-GAC) using the sputtering method and the Ag-GAC was evaluated for the removal of formaldehyde, the target indoor air pollutant at room temperature. The experimental results were compared to those obtained using virgin GAC. The main objective of this research was to examine and quantify the catalytic oxidation by silver nano-particles and the GAC adsorption for practical applications in indoor. In addition, the HSDM was modified to incorporate the catalytic oxidation, and a series of numerical simulations using the modified model (CO-HSDM) was conducted to predict the performance of formaldehyde removal by Ag-GAC. The experimental data collected from test columns packed with either virgin GAC or Ag-GAC were used to calibrate and validate the model.

2. Model development

2.1. Homogeneous surface diffusion model (HSDM)

The HSDM describes the mass transfer and adsorption of target compounds in GAC-packed columns [18]. The target compound, formaldehyde in this study, was mass-transferred by advection along the column and diffusion into the GAC particles as functions of the time and location in the longitudinal direction. The diffusion into the GAC particles was described as a mass flux based on Fick's law. Several assumptions were made for the construction of the model to consider the mass transfer in the air and solid phases, as well as the adsorption onto the solid phase; (1) there was no turbulence and dispersion in the bulk phase column, (2) the solid phase, i.e. GAC, was homogeneous with respect to porosity, density and adsorptive capacity, (3) the advection and dispersion were ignored on the surface of the GAC, and (4) the bulk concentration

of the target compound on the surface of the GAC attains equilibrium with the concentration in the solid phase, and this equilibrium was expressed using the Freundlich isotherm. Based on the above assumptions, the HSDM equations and boundary conditions are given as follows:

$$\text{Column: } \frac{\partial C}{\partial t} = -V_s \frac{\partial C}{\partial z} - \frac{3(1-\varepsilon)J}{\rho R} \quad (1)$$

$$\text{Diffusive flux: } J = D_s \rho_a \left(\frac{\partial q}{\partial r} \right)_{r=R}$$

$$\text{Initial condition: } C = 0 \quad (0 \leq z \leq L) @ t = 0$$

$$\text{Boundary condition: } C = C_0 @ z = 0, t > 0$$

$$\text{Particle: } \frac{\partial q}{\partial t} = -\frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (2)$$

$$\text{Initial condition: } q = 0 \quad (0 \leq z \leq L, 0 \leq r \leq R, t = 0)$$

$$\text{Boundary condition: } \left(\frac{\partial q}{\partial r} \right)_{r=0} = 0$$

$$\text{Freundlich equation: } q_s = KC_s^{1/n} \quad (3)$$

where C is the formaldehyde concentration in the gas phase (mg/m^3), C_0 is the inlet concentration of formaldehyde (mg/m^3), C_s is the formaldehyde concentration at the gas/GAC interface (mg/m^3), ε is the porosity of the GAC bed, V_s is the superficial gas velocity in the column (m/s), q is the adsorptive loading (mg -formaldehyde/ g -GAC), q_s is the adsorptive loading at equilibrium with C_s (mg -formaldehyde/ g -GAC), ρ_a is the apparent density of a GAC particle (g -GAC/ m^3 -GAC volume), D_s is the surface diffusion coefficient (m^2/s), r is the radial position (radial coordinates) in a GAC particle, K and $1/n$ are the Freundlich isotherm parameters ($(\text{mg}/\text{g})(\text{L}/\text{mg})^{1/n}$ and dimensionless, respectively), L is the length of the GAC-packed column (m), and R is the radius of a GAC particle (m).

2.2. Catalytic oxidation and homogeneous surface diffusion model (CO-HSDM)

The adsorption and catalytic oxidation simultaneously occur on the surface of Ag-GAC. Because the HSDM only considers the adsorption, it cannot describe the combined oxidation/adsorption reactions. To overcome this problem encountered with Ag-GAC predictions, modification to the HSDM (CO-HSDM) was attempted to incorporate the catalyst oxidation taking place on the silver nano-particles evenly spread over the surface of Ag-GAC. Since the nano-particles cover some parts of the GAC surface, physically blocking the micro-pores, the adsorptive ability of Ag-GAC may be reduced by the attachment of the nano-particles. The blockage and limited surface availability for adsorption need to be considered in the CO-HSDM. Therefore, additional assumptions were made for the CO-HSDM; (1) the catalytic oxidation by the silver nano-particles only occurs on the surface of Ag-GAC, and the degree of the oxidation is proportional to the fraction of the surface area covered by nano-particles, (2) the oxidation reaction by the silver nano-particles follows first-order kinetics by simplifying the Eley-Rideal kinetic equation [19], (3) the adsorption does not occur at the point where the silver nano-particles were attached and they blocked the diffusion of formaldehyde into the inside of a GAC particle, (4) no intermediates or by-products of the formaldehyde oxidation were produced nor accumulated on either the silver nano-particles or GAC, and (5) catalyst poisoning and declining activity of the silver nano-particles were negligible for a short-term operational period. Based on these additional assumptions, the governing equation for the gas-phase flux can be modified as follows:

$$\frac{\partial C}{\partial t} = -V_s \frac{\partial C}{\partial z} - \frac{3(1-\varepsilon)J(1-\alpha) - k_{Ag} \cdot C \cdot \alpha}{\varepsilon R} \quad (4)$$

Table 1
Model parameters used in the model simulations.

	Parameter	Value	Unit	Determined
Operating parameters	Z (Total column height)	4×10^{-3}	m	This study
	V (Total volume)	3.14×10^{-6}	m ³	
	Q (Gas phase flow rate)	1.256×10^{-5} and 6.283×10^{-5}	m ³ /s	
	RT (Gas retention time)	0.25 and 0.5	s	
	V _s (Gas superficial velocity)	0.059 and 0.029	m/s	
GAC parameters	ε (Porosity of bed)	0.674	–	Provided by manufacturer
	R (Diameter of particle)	1.5×10^{-3}	M	
	ρ _a (Apparent density)	0.76×10^{-3}	kg/m ³	
Experimentally determined	α (Surface coverage fraction)	0.293	–	BET analysis
	k _{Ag} (kinetic coefficient)	0.082	1/s	Oxidation test
	K (Freundlich parameter)	104.41	(mg/g)(L/mg) ^{1/n}	Isotherm test
	1/n (Freundlich parameter)	0.412	–	Isotherm test
Estimated	D _s (Diffusion coefficient)	2×10^{-12}	m ² /s	Model fitting

where α is the fraction of the surface area covered by the silver nano-particles to the entire surface area of the GAC (dimensionless), and k_{Ag} the first-order oxidation constant of the silver nano-particles. The initial and boundary conditions applied to Eq. (4) were the same as those in Eq. (1).

2.3. Model simulation and parameter estimation

The gas phase flux equation (either Eq. (1) for the HSDM or Eq. (4) for the CO-HSDM) and the mass diffusion equation (Eq. (2)) were converted to a paired set of equations using a finite difference explicit scheme for a boundary value problem. The numerical analysis was performed using the MATLAB® software. The parameters used in these model simulations for either the HSDM or CO-HSDM are listed in Table 1. The values of the parameters related to the physical properties of GAC, such as porosity and density, were those given by the manufacturer. The model parameters, including K , $1/n$, k_{Ag} and α , were experimentally determined in this study. However, the surface diffusion coefficient (D_s) was not able to be experimentally determined herein; therefore, numerical estimation for the parameter was performed using a nonlinear best fit method where the difference between the actual experimental data obtained under a given condition and the simulated formaldehyde mass removed was minimized. Since the HSDM and modified CO-HSDM were constructed to predict the performance of GAC and Ag-GAC with respect to the removal of formaldehyde, the accuracy of the simulation was quantified by comparing the total mass of formaldehyde removed until the breakthrough was completed (i.e., $C_{outlet} = C_{inlet}$) in each column test.

3. Materials and methods

3.1. Synthesis of silver nano-particles and Ag-GAC

The GAC used this study was coal-based virgin carbon (Calgon, USA; CPG 8 × 30 mesh) with an averaged diameter of 1.5 mm. The GAC was washed with deionized water and air-dried at 105 °C in an oven before use. The silver nano-particles attached onto the supporting materials were supplied by a nano-material manufacturing company (Plasma & Ion-beam, Inc., Korea). The silver nano-particles were produced by a physical nano-structure coating method that used high-energy argon-ion-beams, which was similar to the method reported in the literature [20,21]. The spherical silver particles on the surface of the GAC were sputter-deposited using an Ar⁺ beam at 2000 eV and with a flow rate of 300 ± 15 mL/min for 30 min. Under vacuum conditions within the sputtering chamber (less than 0.02 Torr), the Ar⁺ beam bombarded pure silver foil and evaporated metallic silver, and then nano-sized particles

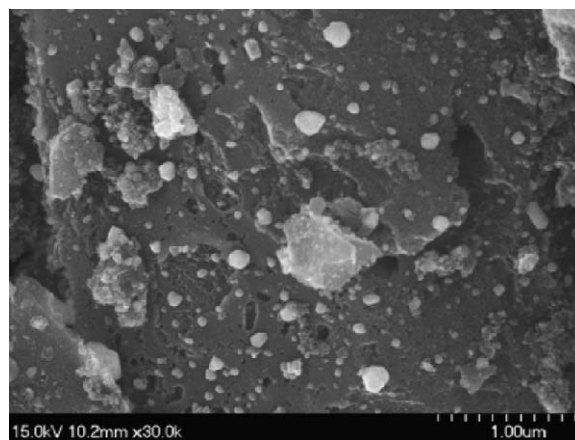


Fig. 1. A SEM image of the silver nano-particle developed on the GAC surface.

were formed on the surface of the supporting materials, which were mixed at 20 rpm. In this study, the final quantity of silver nano-particles attached onto the GAC was 1000 ± 30 mg-Ag/kg-GAC. Fig. 1 shows a scanning electron microscope (SEM) image of the silver nano-particles deposited onto the surface of the GAC manufactured for this study. The SEM image indicates that the sizes of the silver nano-particles ranged from 30 to 150 nm, and the nano-particles were evenly developed on the entire GAC surface. For comparison, instead of using GAC, the same sputtering method and Ag concentration were applied to glass beads with an averaged diameter of 2 mm, with silver nano-particles formed on the surface of the glass beads to determine the catalytic oxidation kinetics without the carbon adsorption.

3.2. Adsorption isotherm

Batch isotherm tests were performed to determine the adsorption capacity of the virgin GAC for formaldehyde in the vapor phase. The isotherm tests were conducted by adding known amounts of virgin GAC ranging from 0.1 to 8 g, and formaldehyde vapor at various gas-phase concentrations into a 25 mL glass bottle equipped with a Teflon-coated septum. The bottles were shaken for 24 h in a tumbler maintained at 25 °C, and then headspace gas samples were taken and analysed for formaldehyde. The adsorption isotherm for the formaldehyde vapor with the GAC was determined using the two-parameter equilibrium adsorption model, the Freundlich isotherm equation (Eq. (3)) with a nonlinear best-fit method.

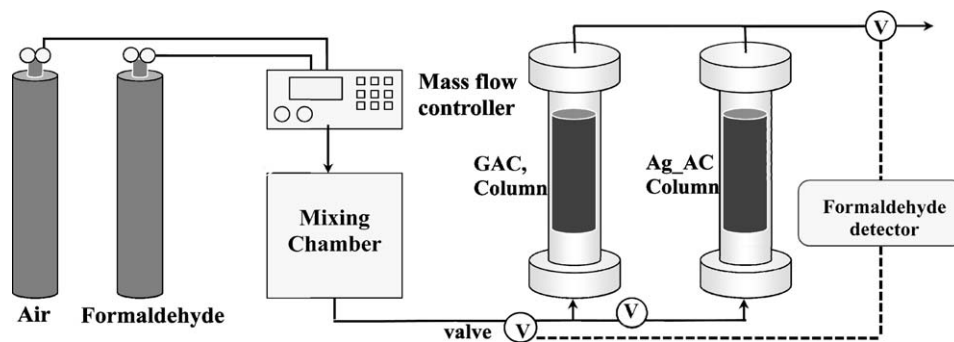


Fig. 2. Schematic of the packed-bed columns.

3.3. Column configuration and operation

The laboratory-scale test units used in this study consisted of stainless steel columns (1.0 cm I.D.) packed with either the GAC or Ag-GAC to a height of 4 cm, as shown in Fig. 2. Research-grade air and formaldehyde vapor streams were regulated using a mass flow controller and mixed in a mixing chamber to obtain a target formaldehyde concentration of 9 ± 1 ppm. For the continuous column tests, the gas flow rates were set at 1.26×10^{-5} and 6.28×10^{-6} m³/s, corresponding to empty bed gas retention times (RTs) of 0.25 and 0.50 s, respectively. The inlet and outlet concentrations of formaldehyde were monitored by directly withdrawing a small fraction of the gas stream to a formaldehyde analyzer. For comparison with Ag-GAC, silver nano-particles attached onto glass beads were manufactured as described above, and packed into the same column. In this glass bead test, the formaldehyde concentration introduced to the column was set at 19 ± 1 ppm. Both the formaldehyde and carbon dioxide concentrations were monitored in the inlet and the outlet streams.

3.4. Analytical methods

The vapor-phase concentration of formaldehyde was measured using gas chromatography equipped with a flame ionization detector (GC/FID, HP 6890, Agilent, USA). The gas samples were collected using a 0.5 mL gas-tight syringe, and analysed immediately by the GC/FID. For the continuous measurement in the column test, an electrochemical formaldehyde analyzer (Model 4000, Interscan, USA) was used, and the results of the formaldehyde analyzer were compared to those of the GC/FID for quality assurance purposes. The carbon dioxide evolved from the oxidation of formaldehyde was monitored using a non-dispersive infrared CO₂ analyzer (LI-820, LI-COR, USA). The BET surface area was determined using a specific surface analyzer (Micromeritics, ASAP-2020, USA), and the BET analysis was conducted at 77 K by nitrogen gas adsorption.

4. Results and discussion

4.1. Adsorption isotherm and specific surface area

Prior to the continuous column tests, a batch isotherm study was performed to determine the adsorption capacities of the virgin GAC for formaldehyde vapor. Equilibrium concentrations in the gas phase (C_e) and absorbed formaldehyde loadings in the GAC (q_e) were used to estimate the Freundlich model coefficients (K and $1/n$) using the nonlinear best-fit method. The Freundlich model coefficient K was determined to be $104.4 \text{ (mg/g)(L/mg)}^{1/n}$, with a $1/n$ value of 0.41 for formaldehyde vapor. The Freundlich isotherm curve illustrated in Fig. 3 satisfactorily reflected the experimental results. Qingbo et al. [22] also reported that the adsorption capacity

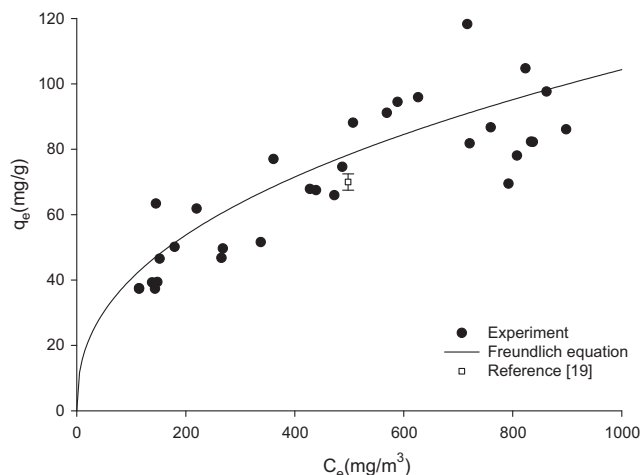


Fig. 3. Formaldehyde adsorption by the virgin GAC and the Freundlich model fitting.

of a commercially available coal-based carbon was 70 ± 2 mg/g at a formaldehyde concentration of 498 mg/m^3 , which was close to the result obtained in this study. Nevertheless, in general, the adsorptive capacity of ordinary GAC for formaldehyde is much smaller than that for toluene, the major pollutant commonly found in indoor air. The same GAC used in this study was tested to determine its adsorptive capacity for toluene. This isotherm test showed that the Freundlich coefficient K was $190 \text{ (mg/g)(L/mg)}^{1/n}$ for toluene (data not shown). Consequently, the use of GAC for indoor air quality control requires careful attention, since the adsorptive capacity for formaldehyde is generally lower than that of other pollutants, and GAC needs to be more frequently replaced for the effective control of formaldehyde in a chemical mixture. To increase the overall removal efficiency and lifetime of the GAC for the removal of formaldehyde, silver nano-particles were deposited onto the surface of the GAC to achieve simultaneous catalytic oxidation.

To investigate the changes in surface properties due to the nano-particle deposition, the specific surface area was determined using the BET method for both GAC and the Ag-GAC. The BET surface areas were found to be $907 \pm 5 \text{ m}^2/\text{g}$ for the virgin GAC and $641 \pm 12 \text{ m}^2/\text{g}$ for the Ag-GAC. In addition, the pore-size distribution data indicated that the total pore volumes remained almost the same, but the micro-pore volume (less than 200 nm) of the Ag-GAC was substantially reduced (data not shown). These findings imply that the deposition of nano-particle reduced the available surface area of the GAC and blocked the openings of micro-pores. Generally, the deposition of metal and/or polymer structures onto GAC can cause a decline in the surface area [23], because the deposits physically block both the outer surface and the openings of pore structures. Lam and Hu also showed [24] that the BET specific surface area and

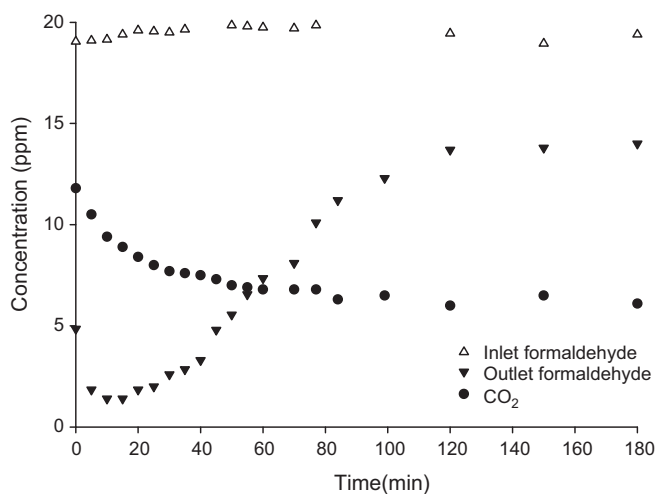


Fig. 4. Catalytic oxidation of formaldehyde and carbon dioxide evolution by silver nano-particles attached onto glass beads.

total adsorption volume of a copper/activated carbon catalyst were reduced from 1052 to 743 m²/g, due to the formation of the copper deposits on the porous media both externally and internally. In this study, a fraction (α) of the surface area covered by the silver nano-particles to the entire surface area was introduced to quantify the surface coverage by the deposition of metallic silver, and the α value was determined by the decline in the BET specific surface area, and was found to be 0.293 for the Ag-GAC.

4.2. Oxidation kinetics for formaldehyde by silver nano-particles

To determine the catalytic oxidation kinetics only, without the carbon adsorption, silver nano-particles were formed on glass beads as described above, with the removed formaldehyde and evolved CO₂ monitored in another column test. As shown in Fig. 4, the experiment result of silver nano-particles attached on the glass beads (Ag-GB) provided clear evidence of the catalytic oxidation of formaldehyde. The vapor-phase inlet concentration of formaldehyde remained constant at 19 ± 1 ppm throughout the column test, and the outlet concentration of formaldehyde gradually increased, reaching approximately 14 ppm in a 120 min period. Approximately 70% of the formaldehyde introduced into the Ag-GB column was catalytically oxidized under the steady-state condition. During the same time period, the CO₂ concentration evolved from the Ag-GB column was initially 12 ppm, but gradually dropped to approximately 6 ppm under the steady-state condition. Considering a one-to-one molar conversion of the formaldehyde oxidation ($\text{HCOH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$), the experimental result implies the almost complete oxidation of formaldehyde to carbon dioxide.

These experimental data of the oxidation of formaldehyde were fitted to the model Eq. (4) described above. The diffusive flux (J) in Eq. (4) was set to zero, since there was no adsorptive mass flux into the glass beads. The comparison of the SEM images of Ag-GB and Ag-GAC showed that the size of the nano-particles was similar with each other (image not shown). The concentration of the Ag deposited on the GB and GAC surfaces was the same at 1000 mg-Ag/kg. Hence, the pseudo-first-order oxidation constant of the silver nano-particles (k_{Ag}) obtained from Ag-GB was directly applied to the CO-HSDM simulation where the Ag-GAC was applied. Using the nonlinear best-fit method, where the square sum of errors between the simulation values and experimental data was minimal, the catalytic reaction constant (k_{Ag}) was determined to be 0.088 s⁻¹, and this constant was used in the model simulations for the Ag-GAC column operations.

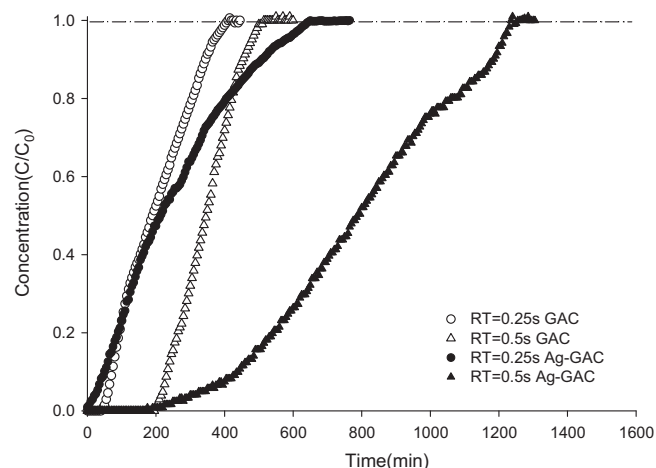


Fig. 5. Formaldehyde breakthrough curves of the virgin GAC and Ag-GAC at two different gas retention times, 0.25 and 0.5 s.

4.3. GAC and Ag-GAC column performance

Fig. 5 illustrates the four sets of experimental results obtained at two different gas RTs, 0.25 and 0.5 s, either in the GAC or Ag-GAC column. Each column operation was terminated when the outlet formaldehyde concentration reached its inlet concentration, which was defined as a complete breakthrough. In the virgin GAC columns, the complete breakthrough occurred at 410 min at the RT of 0.25 s, but was extended to 510 min at the longer RT of 0.5 s. When normalizing the operating time with each corresponding RT (i.e., expressing the x-axis using a dimensionless time known as the bed volumes fed), the two formaldehyde breakthrough curves of the virgin GAC showed similar patterns and were very closely matched. In addition, from the areas of the breakthrough curves, the total masses of formaldehyde absorbed were calculated to be 1.64 and 1.63 mg at the RT values of 0.25 and 0.5 s, respectively. These findings indicated that the GAC adsorption capacity for formaldehyde was unchanged within the gas flow rate range tested.

On the contrary, the Ag-GAC showed much longer breakthrough times than the virgin GAC at the same RTs. The Ag-GAC exhibited complete breakthrough at 630 and 1200 min when operated at the RTs of 0.25 and 0.5 s, respectively. Furthermore, the two breakthrough curves of the Ag-GAC at the different RTs did not show similar shapes, with a slower increase in the outlet formaldehyde concentration observed at the longer RT. The total mass of formaldehyde removed in the Ag-GAC column at the RT of 0.25 s was 2.16 mg, which was 1.3 times higher than that observed in the virgin GAC column at the same RT. In contrast, at the RT of 0.5 s, the mass of formaldehyde removed in the Ag-GAC column was calculated to be 3.94 mg, which was 2.4 times higher than that observed in the GAC column. These results imply that the catalytic oxidation played a significant role in the Ag-GAC column, with an increasing quantity of formaldehyde oxidized with increasing RT.

4.4. Model simulation and validation

The model presented herein was developed to predict the changes in the performance of a GAC column for the removal of formaldehyde vapor as well as the simultaneous oxidation and adsorption occurring in the Ag-GAC. The model parameters used in this study for both the HSDM and CO-HSDM are listed in Table 1. Most of the model parameters were supplied by the manufacturer or experimentally determined as mentioned above. However, the surface diffusion coefficient (D_s) varied substantially depending on temperature and materials tested, and was not able to be exper-

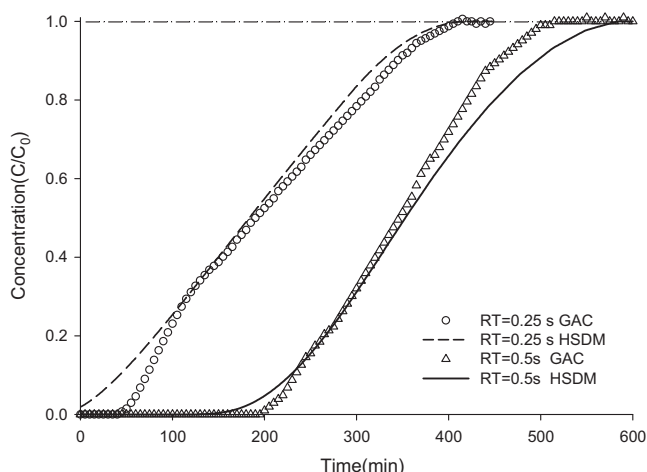


Fig. 6. Simulated results using the HSDM (lines) and the experimental data (symbols) obtained from the GAC column tests.

imentally determined in this study; therefore, it was estimated by fitting the model to the experimental data collected from the virgin GAC column operated at an RT of 0.25 s. A formaldehyde diffusion coefficient of $6.78 \times 10^{-13} \text{ m}^2/\text{s}$, reported by Zhang et al. [25] who tested formaldehyde partitioning and diffusion coefficients for dry building materials, was used as a starting point in the estimation process. The HSDM simulations were iteratively conducted by systematically changing the D_s value to obtain a minimum of the sum of square errors between the simulated mass of formaldehyde adsorbed onto the GAC and the actual mass of formaldehyde removed until the complete breakthrough had been attained in the column test. The estimated D_s was $2.0 \times 10^{-12} \text{ m}^2/\text{s}$, which was used for the HSDM simulation at an RT of 0.5 s as well as for the CO-HSDM simulations at RTs of 0.25 and 0.5 s.

The results of the HSDM simulation using the set of the model parameters were relatively consistent with the experimental data obtained in the GAC columns, as shown in Fig. 6. There were slight deviations between the actual data and the model predictions, especially in the early phase of the formaldehyde breakthrough and near the complete breakthrough points. Since the GAC had a low adsorption capacity for formaldehyde, and the mass transfer zone where the formaldehyde adsorption took place along the length of the column was relatively short, deviations from the model assumptions could be plausible reasons for the discrepancies at the beginning and end phases of the adsorption with these short gas RTs.

The numerical analysis of the CO-HSDM was performed using the same set of the model parameters as used with the HSDM, but with the use of additional parameters including the ratio of the nano-particle coverage ($\alpha = 0.293$) and the pseudo-first-order kinetic constant ($k_{Ag} = 0.088 \text{ s}^{-1}$) as mentioned above. Fig. 7 demonstrates that the results predicted using the CO-HSDM agreed well with experimental data of the Ag-GAC at both RTs. Consequently, the CO-HSDM yielded an accurate prediction of the performance of the Ag-GAC under different operating conditions with the model parameters employed.

Sensitivity analyses were performed on the four experimentally determined parameters (i.e., K , $1/n$, α and k_{Ag}) and one estimated parameter (D_s) in the CO-HSDM to determine those most critical to the model predictions. The impact of each parameter was measured as the change in the total removed mass of formaldehyde when each parameter was increased from its given value by 10%, while maintaining the other model parameters unchanged at the values listed in Table 1. The one-point perturbation results were calcu-

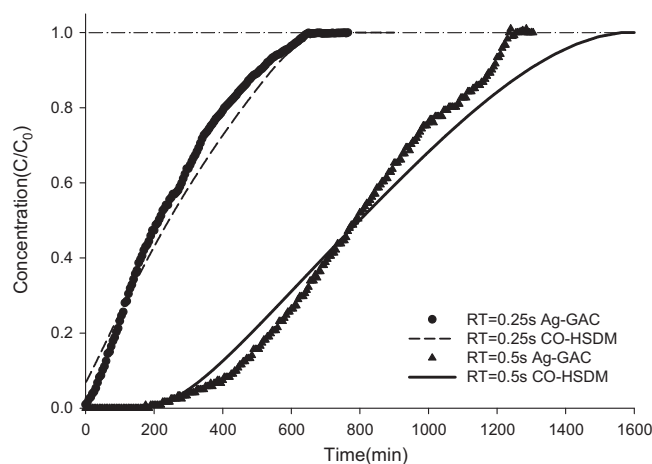


Fig. 7. Simulated results using the CO-HSDM (lines) and the experimental data (symbols) obtained from the Ag-GAC column tests.

lated, and expressed as sensitivity indices (SIs) using the following equation:

$$\text{Sensitivity Index (SI)} = \text{Abs} \left[\frac{\partial f(p)/f(p)}{\partial p/p} \right] \times 100 \quad (5)$$

where p is the particular parameter and $f(p)$ the predicted mass of formaldehyde removed using that parameter. For the sensitivity analysis, an individual SI for each of the five parameters was calculated for the Ag-GAC column tests at the RT of 0.25 s.

The sensitivity analyses indicated that the surface diffusion coefficient (D_s) had the greatest impact (8.7% by the 10% perturbation) on the model predictions. These analyses suggested that an accurate estimate of the surface diffusion coefficient is needed to increase the accuracy of the model predictions. The ratio of the surface coverage (α) by the silver nano-particles to the entire surface area was also found to be a sensitive parameter, with a SI of 5.6% by the 10% perturbation. Since the CO-HSDM relies on the simultaneous oxidation and adsorption reactions, their contributions to the overall removal of formaldehyde are proportional to the α value. Extensive research would be required to obtain more reliable values of D_s and α for model applications.

4.5. Influence of the surface coverage of silver nano-particles

The α value is one of the most important parameters for differentiating the adsorption of the GAC from the catalytic oxidation of the Ag-GAC. The Ag-GAC possesses no oxidation potential as the α approaches zero; whereas, an α of 1 means complete coverage of the GAC surface by a thin film of silver. Model predictions for calculating the overall mass of formaldehyde removed by the Ag-GAC were conducted with various α values ranging from 0 to 0.6, while maintaining the other parameters unchanged. The mass of formaldehyde removed by either the adsorption or the oxidation was separately quantified in the CO-HSDM. As illustrated in Fig. 8, with increasing α value, the mass of formaldehyde removed by adsorption gradually decreased, but the mass of formaldehyde removed by the oxidation rapidly increased. Moreover, the overall mass of formaldehyde removed by the Ag-GAC increased with increasing α value. Interestingly, at an α value of 0.293, which was experimentally determined for the Ag-GAC used in this study, the CO-HSDM predicted that the mass of formaldehyde removed by oxidation was 1.11 mg, which was almost identical to that removed by adsorption. When the α value was set to zero, the mass of formaldehyde removed by adsorption was 1.56 mg, which was consistent with the experimental data obtained with the GAC.

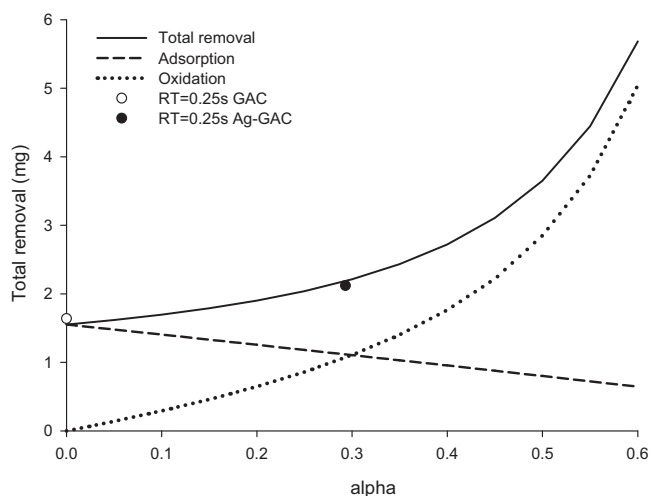


Fig. 8. Predicted profiles for the mass of formaldehyde removed by the catalytic oxidation and the adsorption as a function of the surface coverage ratio (α) of the silver nano-particles.

When the α value increases to greater than 0.5, the overall mass of formaldehyde removed by the Ag-GAC exponentially increased due to increased oxidation. However, at high α values, there would be a strong possibility that the silver structures no longer exist as nano-particles on the GAC surface, but would more likely form a thin coating as a film-like layer. Consequently, the CO-HSDM developed in this study could be a useful tool for determining the extent of nano-sized metal deposits required to maximize the catalytic oxidation on the surface of adsorptive materials such as GAC and carbon fibers.

5. Conclusions

This study was conducted to investigate the effects of silver nano-particles attached onto the surface of GAC on the simultaneous catalytic oxidation and adsorption reactions of formaldehyde, the most common pollutant found in indoor air. The experimental results were compared with those collected using ordinary virgin GAC. In addition, the homogeneous surface diffusion model (HSDM), developed for predicting GAC column adsorptions, was modified to incorporate the catalytic oxidation that takes place on the Ag-GAC surface. The key observations and specific conclusions drawn from this research are as follows:

1. The isotherm tests showed that gaseous formaldehyde was effectively removed by its adsorption into and onto the GAC. However, the adsorptive capacity of the GAC for formaldehyde was much lower than those for other pollutants found in indoor air; therefore, additional technologies would be required to achieve the effective control of formaldehyde.
2. The catalytic oxidation conducted using the silver nano-particles formed on the glass beads implied that approximately 70% of the formaldehyde introduced was oxidized under steady-state conditions, and the same molar concentration of oxidized formaldehyde was converted to carbon dioxide. In addition, the oxidation kinetics was expressed as pseudo-first-order with a kinetic constant of 0.088 s^{-1} .
3. The Ag-GAC showed much longer breakthrough times in the column tests than the virgin GAC at the same RTs. The mass of formaldehyde removed by the Ag-GAC column was 2.4 times higher than that observed in the GAC column at an RT of 0.5 s. The catalytic oxidation was observed to play a significant role in

the Ag-GAC, where the quantity of formaldehyde oxidized was increased with increasing RT.

4. The BET specific surface area measurements indicated that the nano-particle deposits reduced the available surface area of the GAC and blocked the openings of the micro-pores. The fraction (α) of the surface area covered by the silver nano-particles to the entire surface area was found to be an important parameter for differentiating the adsorption by the GAC from the catalytic oxidation by the Ag-GAC.
5. The model predictions using the modified HSDM agreed well with the experimental data collected from the column tests at the two different RTs, suggesting that the CO-HSDM yielded an accurate prediction of the performance of the Ag-GAC under different operating conditions with the model parameters employed. The sensitivity analyses indicated that the surface diffusion coefficient (D_s) and the ratio of surface coverage (α) by the silver nano-particles had the greatest impacts on the model predictions. Accurate estimates of these parameters are required to increase the reliability of the model predictions.
6. As the α value increased, the overall mass of formaldehyde removed by the Ag-GAC increased due to the rapid increase in the fraction of catalytic oxidation, but the fraction of the mass of formaldehyde removed by the adsorption gradually decreased.

The Ag-GAC showed a significantly improved formaldehyde removal performance than that of the general GAC. Additional studies should be conducted on (1) the method to minimize the decrease of the Ag-GAC adsorption capacity following nano-particle deposition, (2) the method to reactivate the catalytic effect of Ag when the performance of the Ag-GAC decreases by a long-term use of Ag-GAC, and (3) the evaluation of the temperature change considering the extension of the Ag-GAC applicability under various conditions. A higher practical applicability and feasibility may be able to be secured on the basis of the result of these future studies.

References

- [1] P.O. Jeffrey, S.F. Lim, Airborne concentrations of bacteria in a hospital environment in Singapore, *Water, Air Soil Pollut.* 144 (2003) 333–341.
- [2] World Health Organization, WHO Guidelines for Indoor Air Quality: Selected Pollutants, WHO Regional Office of Europe, 2010.
- [3] J. Pei, J.S. Zhang, On the performance and mechanisms of formaldehyde removal by chemi-sorbents, *Chem. Eng. J.* 167 (2011) 59–66.
- [4] K.J. Lee, N. Shiratori, G.H. Lee, J. Miyawaki, I. Mochida, S. Yoon, J. Jang, Activated carbon nanofiber produced from electrospun polyacrylonitrile nanofiber as a highly efficient formaldehyde adsorbent, *Carbon* 48 (2010) 4248–4255.
- [5] S. Tanada, N. Kawasaki, T. Nakamura, M. Araki, M. Isomura, Removal of formaldehyde by activated carbons containing amino groups, *J. Colloid Interface Sci.* 214 (1999) 106–108.
- [6] C.G. Granqvist, A. Azens, P. Heszler, L.B. Kish, L. Osterlund, Nanomaterials for benign indoor environments: electrochromics for “smart windows”, sensors for air quality, and photo-catalysts for air cleaning, *Sol. Energy Mater. Sol. Cells* 91 (2007) 355–365.
- [7] S. Bashkova, D. Deoki, T.J. Bandosz, Effect of silver nanoparticles deposited on micro/mesoporous activated carbons on retention of NO_x at room temperature, *J. Colloid Interface Sci.* 354 (2011) 331–340.
- [8] I. Piwonska, K. Kadziola, A. Kisielewska, K. Soliwodaa, M. Wolszczakb, K. Lisowskac, N. Wronskac, A. Felczak, The effect of the deposition parameters on size, distribution and antimicrobial properties of photoinduced silver nanoparticles on titania coatings, *Appl. Surf. Sci.* 257 (2011) 7076–7082.
- [9] N.H. Hiroshi, Z.M. Hu, N. Hiromi, Theoretical studies on the catalytic activity of Ag surface for the oxidation of olefins, *Int. J. Quantum Chem.* 65 (1998) 839–855.
- [10] S.C. Kim, J.Y. Ryu, Properties and performance of silver based catalysts on the catalytic oxidation of toluene, *Environ. Technol.* 32 (2011) 561–568.
- [11] G.K. Borekov, Oxygen adsorption and the reaction of the adsorbed oxygen with molecular hydrogen on silver films, *Vacuum* 177 (1967) 145–148.
- [12] M.F. Luo, X.X. Yuan, X.M. Zheng, Catalyst characterization and activity of Ag–Mn, Ag–Co and Ag–Ce composite oxides for oxidation of volatile organic compounds, *Appl. Catal. A: Gen.* 175 (1998) 121–129.
- [13] C.B. Wang, G.D., I.E. Wachs, Interaction of polycrystalline silver with oxygen, water, carbon dioxide, ethylene, and methanol: in situ Raman and catalytic studies, *J. Phys. Chem. B* 103 (1999) 5645–5656.
- [14] S. Kato, Y. Hirano, M. Iwata, T. Sano, K. Takeuchi, S. Matsuzawa, Photocatalytic degradation of gaseous sulfur compounds by silver-deposited titanium dioxide, *Appl. Catal. B: Environ.* 57 (2005) 109–115.

- [15] D. He, A.M. Jones, S. Garg, A.N. Pham, T.D. Waite, Silver nanoparticle-reactive oxygen species interactions: application of a charging-discharging model, *J. Phys. Chem. C: Nanomater. Interface* 115 (2011) 5461–5468.
- [16] A.M. Jones, S. Garg, D. He, A.N. Pham, T.D. Waite, Superoxide-mediated formation and charging of silver nanoparticles, *Environ. Sci. Technol.* 45 (2011) 1428–1434.
- [17] J.C. Crittenden, W.C. Wever jr., Predictive model for design of fixed-bed adsorbers: parameter estimation and model development, *Environ. Eng.* 104 (1978) 185–197.
- [18] J.C. Crittenden, W.C. Wever jr., Predictive model for design of fixed-bed adsorbers: single component model verification, *J. Environ. Eng.* 104 (1978) 433–443.
- [19] P. Hurtado, S. Ordóñez, H. Sastre, F.V. Diez, Development of a kinetic model for the oxidation of methane over Pd/Al₂O₃ at dry and wet conditions, *Appl. Catal.: B Environ.* 51 (2004) 229–238.
- [20] C.X. Wang, Z.Q. Chen, L.M. Guan, M. Wang, Z.Y. Liu, P.L. Wang, Fabrication and characterization of graded calcium phosphate coatings produced by ion beam sputtering/mixing deposition, *Nucl. Instrum. Methods Phys. Res.* 179 (2001) 364–372.
- [21] J. Ghatak, B. Sundaravel, K.G.M. Nair, P.V. Satyam, Flux dependent 1.5 MeV self-ion beam-induced sputtering from gold nanostructured thin films, *J. Phys. D: Appl. Phys.* 41 (2008) 1–9.
- [22] W. Qingbo, L. Caiting, C. Zhihong, Z. Wei, G. Hongliang, C. Lijun, Z. Guangming, S. Xin, Z. Yapei, Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde, *Bioresour. Technol.* 102 (2011) 942–947.
- [23] A.H. El-Sheikha, A.P. Newman, H. Al-Daffaeea, S. Phull, N. Cresswell, S. York, Deposition of anatase on the surface of activated carbon, *Surf. Coat. Technol.* 187 (2004) 284–292.
- [24] F.L.Y. Lam, X. Hu, A new system design for the preparation of copper/activated carbon catalyst by metal-organic chemical vapor deposition method, *Chem. Eng. Sci.* 58 (2003) 687–695.
- [25] Y. Zhang, X. Luo, X. Wang, K. Qian, R. Zhao, Influence of temperature on formaldehyde emission parameters of dry building materials, *Atmos. Environ.* 41 (2007) 3203–3216.