Thesis for the Degree of Master of Engineering

The study for removal of TMA and H_2S using metal loaded on cocoa activated carbon

by

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UR Interdisciplinary Program of Mechanical Engineering

Graduate School

Pukyong National University

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(금속이 부착된 코코아 활성탄을 사용한 TMA 와 H_2S 의 제거에 관한 연구)

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by

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Abstract

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제한된 공간인 경우, 트리메틸아민 (TMA) 및 황화수소 (H_2S) 독성 가스에 과도하게 노출되는 것은 매우 위험하다. 오염 물질을 흡착 · 제거하기 위하여 금속 촉매가 부착된 코코아 활성탄 필터를 개발하였다. 활성탄은 다공성 및 높은 비표면적 때문에 유독성 오염 가스 흡착에 광범위하게 사용되고 있다. 본 연구는 밀폐된 공간에서 구리 촉매가 부착된 코코아 활성탄(Cu/AC) 필터를 사용하여 TMA 와 H_2S 의 제거에 관한 연구를 수행하였다. 초기 농도 400 ppm 의 TMA 와 H_2S 를 밀폐된 공간에 주입하고, 구리 촉매가 부착된 코코아 활성탄(Cu/AC) 필터는 TMA 30 분, H_2S 15 분 동안에 완전히 흡착되었다. 또한 흡착 성능을 잘 이해하기 위하여 isotherm 과 kinetic 모델을 적용하였다. TMA 와 H_2S 의 흡착은 Langmuir isotherm 과 좋은 일치를 나타내었으며, pseudo first order 와 pseudo second order 역시 각각 적합하였다. TMA 와 H_2S 의 흡착은 intraparticle diffusion 과 Yoon-Nelson kinetic 모델에 일치하였다. H_2S 흡착된 Cu/AC 필터는 재활용

가능하였지만, TMA 흡착된 Cu/AC 필터는 재활용 할 수 없었다. 따라서 구리가 부착된 코코아 활성탄 필터는 실내 공기 정화에 적용 가능함을 알 수 있었다.

Keyword: Cocoa Activated carbon; Adsorption; TMA (Trimethylamine); H_2S (Hydrogen sulfide); Isotherm and kinetic models

1. Introduction

Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature. Their high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air, a trait known as volatility. Materials that cause odor among VOCs had a mercaptans, amines and the others (substance of irritating properties). These materials were determined a degree of odor by the mixing ratio. Japan enacted the odor prevention act in 1973. Korea enacted the odor prevention act in 2005. However, the world population is growing at an average rate of 2% each year. The forecast is that there will be 9 billion of us by 2050. This means more and more mouths to feed year after year. The environment is becoming getting worse. Especially, the toxic gases of TMA and H_2S occurring in the home or factory became a worse living conditions. Particularly, the toxic gases (TMA and H_2S) have seriously threatened the health of people in the confined space. Thus, in this work, a removal of TMA and H_2S technique will be estimated to prevent human health from TMA and H_2S in the confined space.

Trimethylamine (TMA) of $N(CH_3)_3$ is a colorless volatile organic

compound with a strong rotting fish malodor. It is a flammable tertiary amine gas at room temperature and is very soluble in water and other organic solvents. TMA mainly results from the decomposition of plants, animals, fish, and sewage, which is the main agent for the odor often associated with rotting fish, some infections, and awful breath [1-3]. Moreover, it was reported that TMA can cause a variety of diseases on human such as lung toxicity, neurotoxicity, and bad breath [2]. Hydrogen sulfide (H_2S) is a colorless chemical compound with a rotten egg malodor. It is very toxic and highly corrosive gas at the room temperature resulted from anaerobic digestion of sulfate-laden waste streams such as paper, tanning, fermentation, citric acid, mining and so on [4-6]. Hydrogen sulfide can lead to equipment and pipe corrosion and catalysts poisoning due to its highly corrosivity and toxicity. Furthermore, it can not only cause eye irritation at low concentration, but also can paralyze olfactory nerve, even lead to pulmonary edema and possible death [7-10]. Therefore, in order to remove the toxic gases of TMA and H_2S, numerous techniques have been studied and have widely used in industries and commercial sector. For examples, some traditional technologies such as adsorption, liquid adsorption, and membrane separation [11]. Physical adsorption such as activated carbon, zeolites and alumina; chemical decomposition and oxidation [12]; biological oxidation such as bioscrubber, biofiltration and biotrickling filter

[5,13,14]. However, amongst above numerous physical, chemical, biological techniques, activated carbon is considered as a promising method for removal of TMA and H_2S due to its low cost and high efficiency, convenient application, simple and practical design, and vast resources [15]. Currently, among the many resources of activated carbon, cocoa shell has been widely used to make activated carbon for its cost-efficiency, high production, and high carbon content. Cocoa shell is a residue that account for 80% of the dry weight of all cocoa fruit [16], cocoa production was approximately 4.8 million tons worldwide in 2012 [17]. Moreover, cocoa shell mainly composed of pectic polysaccharides (45%), hemicelluloses (20%), cellulose (35%) and contained Klason lignin [18]. So, cocoa shell is very to suit to make high-quality activated carbon and has been widely used on sorption of pollutants. Such as, Saucier et al. represented the removal of sodium diclofenac and nimesulide from aqueous effluents by using activated carbon from cocoa shell [19]. The removal of reactive violet was conducted during 5 day from solutions by cocoa shell activated carbon [20]. De luna et al. used cocoa activated carbon to remove the sodium diclofenac from aqueous [21] and so on. However, to the best of our knowledge, very few studies were conducted for gas phase contaminants such as VOC and H_2S using cocoa activated carbon. Thus, in this paper, we will research the removal of TMA and H_2S using cocoa activated carbon. Furthermore, in order to improve the

removal efficiency of TMA and H_2S, the adsorption of TMA and H_2S also are evaluated using a metal loaded on cocoa activated carbon.

To the best of our knowledge, little study has been performed on the air purification by removing TMA and H_2S gases in a confined space using metal loaded AC (activated carbon) filter. Therefore, more comprehensive studies regarding the removal toxic gases are in need. The specific objective of this study were a) to evaluate the effectiveness of adsorption of TMA and H_2S using cocoa activated carbon (AC) and copper loaded cocoa activated carbon (Cu/AC), b) to devise adsorption isotherms and kinetic models to understand and optimize the adsorption process, and c) to find the regeneration condition for the used filter catalyst.

2. Materials and experiment methods

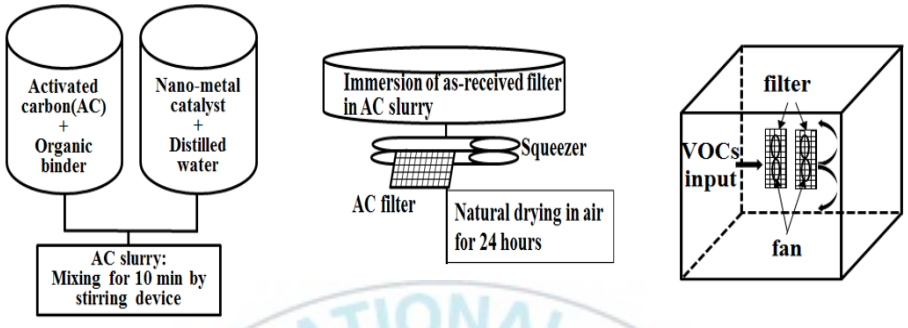
2.1. Sample preparation

The concentration of TMA and H_2S were measured using a PET filter (70 x 70 mm). The PET filter contained a mixture of cocoa activated carbon (Hanil Green Co., Ltd. Korea) 22 wt.%, functional nano-metal catalyst 22 wt.%, organic binder 34 wt.% and distilled water 22 wt.%. The BET specific surface area of cocoa activated carbon is 1031 m^2/g. The TMA and H_2S were chosen as adsorbates for the adsorption of pollutants on cocoa activated carbon filter.

The activated carbon slurry attached to the filters were prepared as follows. First, activated carbon and a binder were mixed, and the catalyst was dissolved in distilled water. The activated carbon slurry was prepared by mixing well for 10 minutes with the dissolved catalyst using a stirrer.

The PET filter was immersed in the activated carbon slurry, and passed through a squeezer, then cured naturally for 24 hours in the air at room temperature as shown in Fig. 1 (a) and (b). Then the air dried filter was cured at 90 ^oC oven for 20 minutes. The optimized curing conditions of temperature and the curing time were determined from a

previous work [22]. The impregnated copper was then identified by using EDS analysis using SEM-EDS (Hitachi S-2400 with Kevex Ltd, Sigma)



(a) (b) (c)

Fig. 1. Schematic diagram of (a) carbonization and activation process, (b) PET ARH filter process, and (c) Toxic gas removal experimental setup.

2.2 Adsorption experiments

An enclosed chamber (0.1 m^3) was chosen for the TMA and H_2S removal study to investigate the removal efficiency of TMA and H_2S in an enclose area as shown in Fig. 1 (c). The produced carbon filter was fixed into an enclosed chamber with conditions of 60% humidity and 20 ^oC. One liter of standard gas (H_2S 4.02% and N_2 balance; Rigas, Korea) was injected in the enclosed chamber to match the

initial H_2S concentration about 400 ppm for all the adsorption experiment. For TMA (TMA30% mixed in water; Junsei Chemical Co., Ltd. Japan), 345 μL of TMA liquid was loaded on the hot pad for complete evaporation in the enclosed chamber to set the initial TMA concentration of 400 ppm. The prepared cocoa activated carbon filter was loaded on the electric fan (80 × 80 mm), and then was operated at a flow velocity of 4.8 m/s until the TMA and H_2S removal was close to 0 ppm (TMA for 30 min and H_2S for 15 min). After adsorption tests, the used Cu/AC filters for TMA and H_2S removal were regenerated in an air drying oven at 200 ºC for the adsorbed pollutant gas removal. Three regeneration residence times (10, 20, and 30 min) were selected to evaluate the effect of residence time on the adsorption of TMA and H_2S performance at the same experimental condition explained above. All the adsorption tests were performed at least duplicate and more, and the average values are reported in the result section.

2.3 Analytical methods

The activated carbon was analyzed using the following analytical methods. The surface morphology of activated carbon sample was observed using FE-SEM (Scanning Electron Microscope; TESCAN

(Czech), VEGA). The impregnated copper was identified with SEM-EDS (Hitachi S-2400 with Kevex Ltd., Sigma). The proximate analysis of carbon was done to determine the VCM (Volatile Combustible matter), FC (Fixed Carbon), and ash contents in accordance with ASTM D3173, D3175, and E1755. The elemental data of C, H, N, and S were analyzed using a Flash 2000 CHNS/O elemental analyzer (Thermo Fisher Scientific). The thermogravimetric analyzer (TCA 7, Perkin Elmer, USA) was used to quantify the volatization properties of cocoa activated carbon. The concentration of H_2S and TMA were measured by a syringe type detector equipped with a detector tube (GasTec Enterprises, Inc.). All analyses were made at least duplicate for the precise analysis. The actual adsotption capacity of the activated carbon filter was measured as given in Equation (1).

$$\text{Sorption capacity } \left(\frac{\text{mg,adsorbate}}{\text{g,adsorbent}}\right) = \frac{V_C}{w} \times \frac{MW}{V_M} \times (C_i - C_f) \quad (1)$$

where V_c (m^3): experimental chamber

w (g): weight of sorbent

MW (34 or 59.11 g/mol): H_2S or TMA molar mass

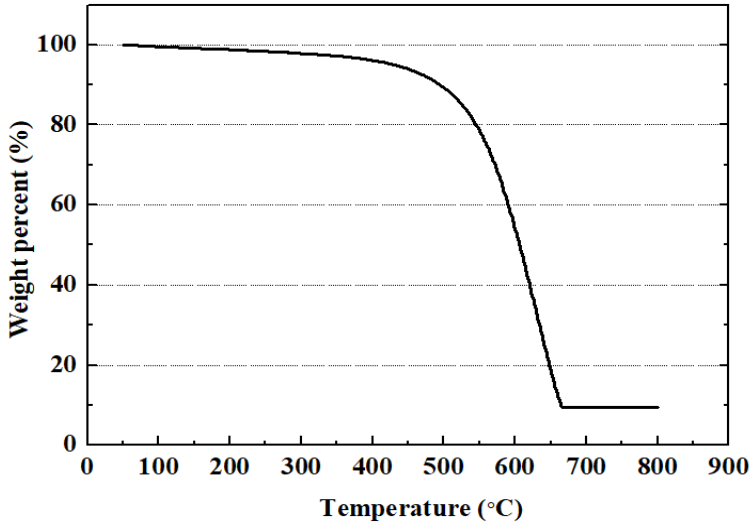
V_m (24 l/mol): molar volume of gas at 20 °C

$C_{i\ or\ f}$ (ppm): initial or final concentration of VOCs

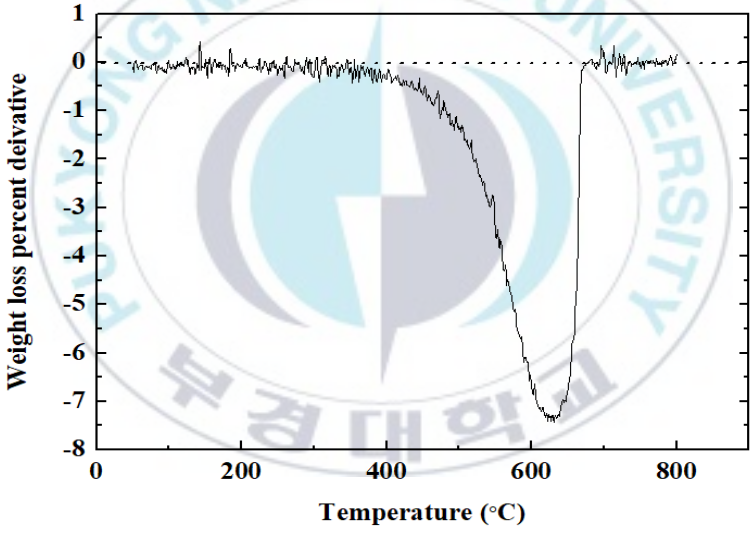
3. Results and Discussions

3.1 Characterization of the adsorbents

The TGA in Fig. 2 (a) shows that the weight of AC began to decrease sharply since the temperature went up to about 500 ^{o}C, and weight of AC sample over the increasing temperature reduced almost 90%. Especially, the decrease rate of weight was up to the maximum at the temperature of 630 ^{o}C as shown in the Fig. 2 (b), and the weight of AC maintained constant after around 680 ^{o}C. The DTG in Fig. 2 (b) also shows the decrease rate of the AC has been constantly changing from about 350 ^{o}C to 680 ^{o}C, and the decrease rate was almost 0 in other temperature ranges. This indicates that the lignin and ash were mostly left over after carbonization and activation process.



(a)



(b)

Fig. 2. TGA and DTG of the cocoa activated carbon

Proximate analysis for VCM (volatile combustible matters), FC (fixed carbon), and ash content was conducted to understand the property changes through carbonization and KOH activation process as shown in Table 1. FC content of cocoa AC was equal to the ARH-450@750, VCM and Ash also was close to the ARH-450@750. On the other hand, FC content of cocoa AC was higher than the others, while VCM and Ash were lower than the others. Three types of ARH were used to be made in our laboratory [36], and used them to do the test of VOCs adsorption, ARH-450@750 showed optimum adsorption performance due to higher FC and lower VCM and Ash from the previous works. However, the elemental analysis presented cocoa AC was different from ARHs, the C content of Cocoa AC was much lower than the others, while H, N, O contents of cocoa AC were higher than the others, which followed the previous conclusion as show in Fig. 2. This indicates that much lignin and ash were mostly left over after carbonization and activation process. We can improve the H/C and O/C ratio through dehydration and decarboxylation to enhance performance of cocoa AC as show in Fig. 3.

Table 1. Proximate and elemental analysis of cocoa AC, rice husk, CRH, and ARHC

	VCM	FC	Ash	C	H	N	O*
Cocoa AC	7.1	83.1	9.8	46.7	5.8	1.2	36.5
ARH-350 @750	10.4	78.3	11.2	67.1 ±0.1[d]	2.3 ±0.14[d]	0.39 ±0.07[b]	18.9
ARH-450 @750	7.4	83.1	9.5	80.7 ±0.2[e]	0.6 ±0.05[e]	0.27 ±0.02[b]	9
ARH-550 @750	9.4	77	13.6	77.3 ±0.5[f]	1.0 ±0.19[f]	0.44 ±0.27[b]	7.7

[a]Values in the same rows with the same letter (a,b or c) are not statistically different (P>0.05).

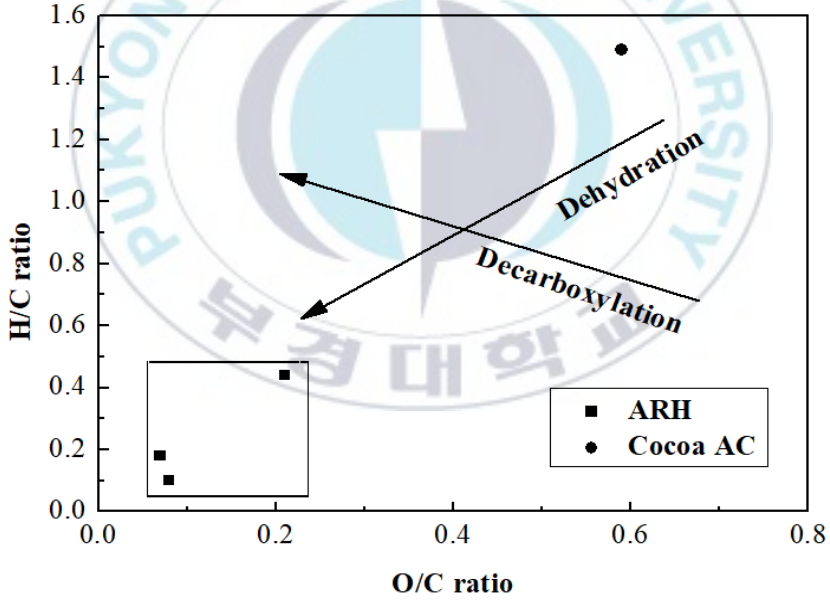
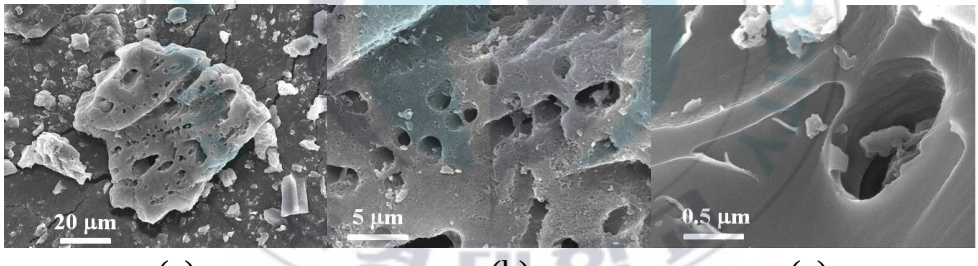


Fig. 3. Van Krevelen diagram of cocoa AC and ARH (activated rice husk)

Fig. 4 Shows SEM images of the cocoa activated carbon. The surface morphology of cocoa activated carbon showed very clear and so many pores were observed clearly. Numerous similar size pores evenly distribute on the cocoa activated carbon surface as show in Fig. 4 (b). A large amount of open pores provides a lot of room for copper impregnation and pollutant gas as show in Fig. 4 (c). The specific surface of cocoa activated carbon is 1031m^2/g from the BET test of cocoa activated carbon. Activated carbon has been widely applied on adsorption of toxic gases and waste water and so on due to the large surface area can adsorb impurities with loaded catalyst on the activated carbon.

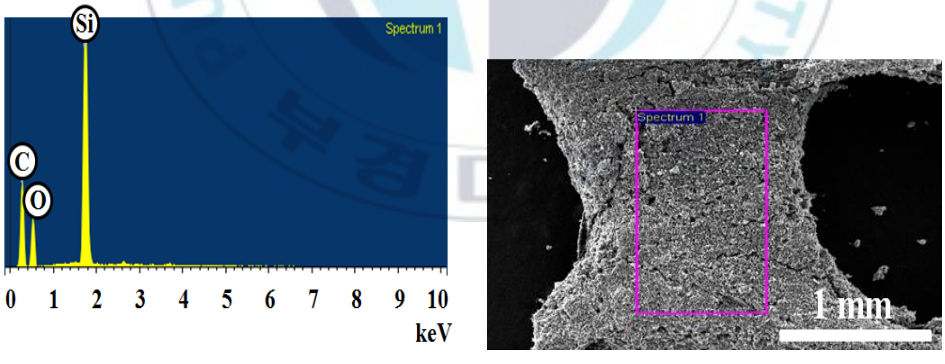


(a) (b) (c)

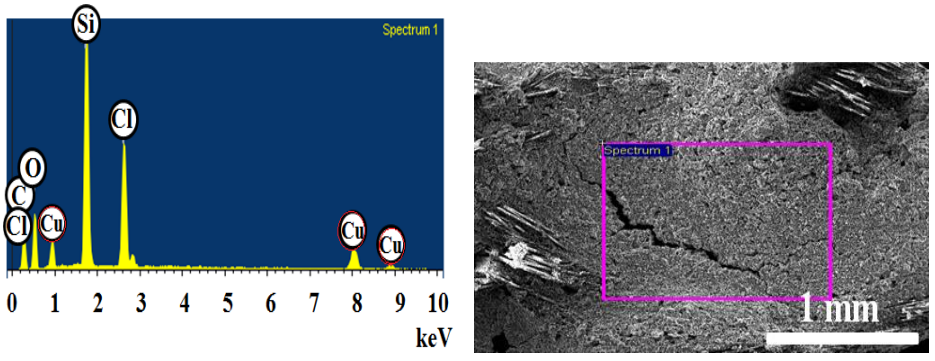
Fig. 4. SEM of cocoa activated carbon.

The SEM-EDS analysis was performed with AC and Cu/AC samples before TMA and H_2S removal to determine the presence of copper as show in Fig. 5 (a) and (b). The EDS peaks indicated the presence of copper with Cu/AC in Fig. 5 (b). In addition, SEM-EDS

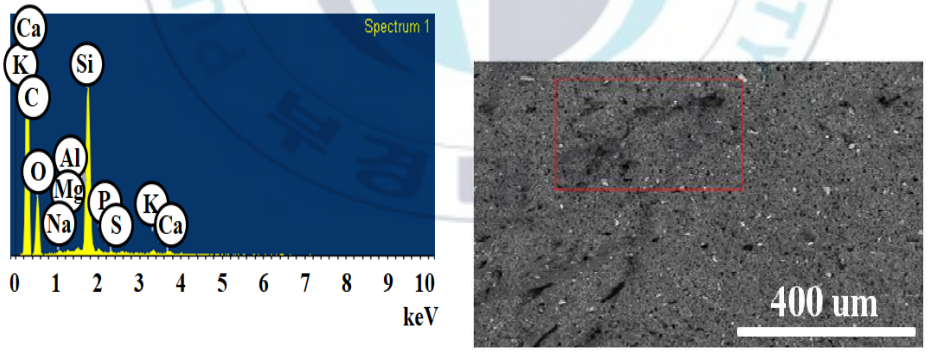
analysis also was performed with AC and Cu/AC samples after TMA and H_2S removal to determine the presence of TMA and H_2S. Fig. 5 (c) and (d) clearly represented that the less pores on the surface of Cu/AC due to most of pores were filled with TMA pollutant. Moreover, the EDS peak of sulfur with Cu/AC was much higher than that one with AC, which indicated that much more H_2S was adsorbed by Cu/AC filter in the existence of copper, followed the SEM that many big pores can be observed clearly, whereas no big pore and much wheat area (sulfur) attached on the Cu/AC surface as shown in Fig. 5 (e) and (f). So, that is, the adsorption of TMA and H_2S had the best performance using copper catalyst loaded on activated carbon.



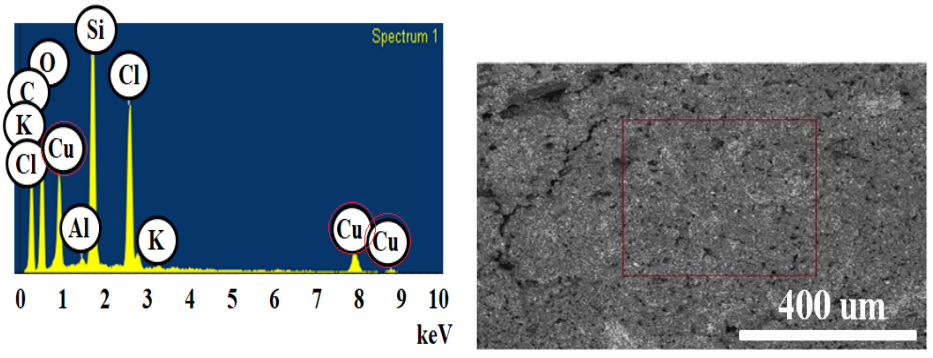
(a) AC



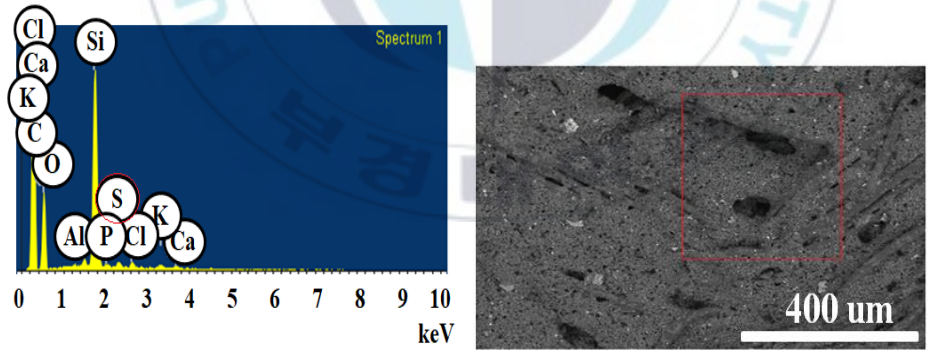
(b) Cu/AC



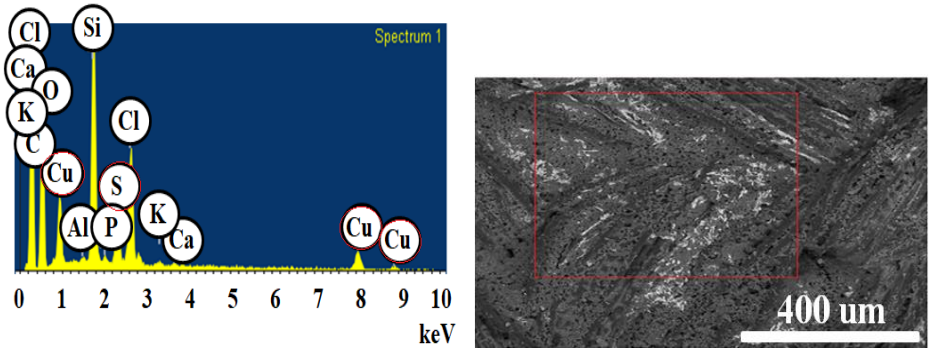
(c) AC after TMA removal



(d) Cu/AC after TMA removal



(e) AC after H_2S removal



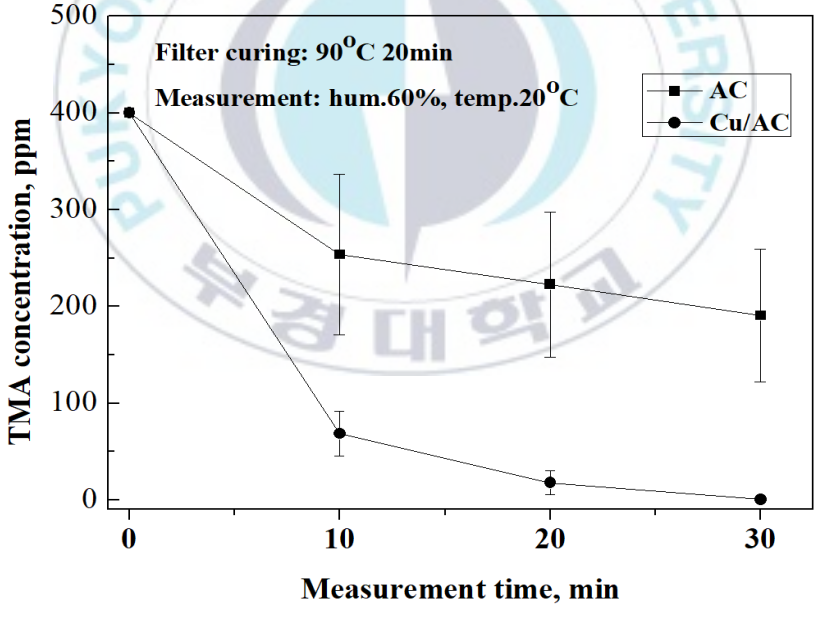
(f) Cu/AC after H_2S removal

Fig. 5. SEM-EDS analysis of (a) AC, (b) Cu/AC, (c) AC after TMA removal, (d) Cu/AC after TMA removal, (e) AC after H_2S removal and (f) Cu/AC after H_2S removal.

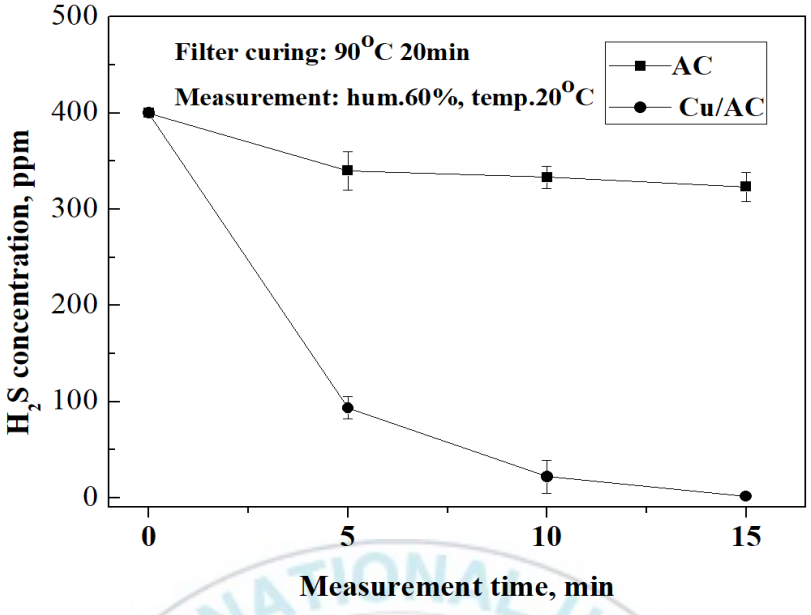
3.2 Adsorption of TMA and H_2S

The adsorption of toxic gases (TMA and H_2S) was carried out with the metal loaded on the cocoa activated carbon in a closed system at 20 ºC and 60% humidity. Initially, adsorption of TMA and H_2S was performed by the cocoa activated carbon without metal catalyst. About 50% reduction in TMA concentration was observed, however, 20% reduction in H_2S was achieved after 15 minutes as show in Fig. 6 (a) and (b). After copper impregnation on the carbonized sample, the TMA concentration decreased to 68 ppm at 10 min, 17 ppm at 20 min and about 0 ppm at 30min. which followed the

sequence of the SEM-EDS as show in Fig. 5 (c) and (d). When it comes to H_2S concentration with Cu/AC filer, 400 ppm concentration was reduced to 93 ppm at 5 min, 22 ppm at 10 min and close 0 ppm at 15 min. This clearly showed that the presence of metal copper catalyst on the high surface area activated carbon increased the removal performance.



(a)



(b)

Fig. 6. VOCs concentration of AC and Cu/AC catalyst.
(a) TMA, (b) H_2S

3.3 Adsorption isotherm studies

In order to optimize the adsorption process, it is crucial important to describe how much adsorbate was adsorbed by a given amount of adsorbent. The equilibrium data was analyzed using Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes that monolayer adsorption happened at adsorption sites with homogenous energy levers, no interactions and no transmigration occurred on the adsorption surface

[23]. The Langmuir equation is represented as following Eq (2).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where C_e (mg/L): equilibrium concentration of pollutant gas
q_e (mg/mg): adsorption capacity at equilibrium
K_L (L/mg): constant value related to free energy of adsorption
q_m (mg/mg): the maximum adsorption capacity at monolayer coverage

The Freundlich isotherm is an empirical equation that assumes the adsorption process occurs on the heterogeneous surfaces at varying energy levels. The n value obtained from Freundlich isotherm model constant indicates whether the adsorption process is physical (n >1), chemical (n < 1), or combination of both (n = 1). The adsorption of the dye using activated carbon is the typical physical adsorption (n>1), indicating that activated carbon has a high degree of heterogeneity [24,25]. The Freundlich isotherm is given as Eq. (3)

$$q_e = K_F C_e^{1/n} \quad (3)$$

where C_e (mg/L): equilibrium concentration of pollutant gas
q_e (mg/g): adsorption capacity at equilibrium
K_F (mg/g(1/mg)$^{1/n}$): relative adsorption capacity
n: affinity of the adsorbate to the adsorbent

Table 2. Correlation parameters for Langmuir and Freundlich adsorption isotherms

		TMA		H_2S	
Isotherm model	parameter	value	R^2	value	R^2
Langmuir	K_L	38.9696	0.9995	980.0367	0.9976
	q_m	670		217.1	
Freundlich	K_F	1.0573	0.9256	0.228	0.9483
	n	2.9735		11.3122	

Table 2. shows the correlation coefficient value R^2 and isotherm constants, comparing the R^2 values, the R2 of 0.9995 provided by Langmuir is higher than R2 of 0.9256 from.

Freundlich mode for TMA Which indicated Langmuir isotherm model is the best fit in describing the adsorption of TMA onto cocoa activated carbon. For H_2S adsorption, the correlation coefficient value R^2 (0.9976) of Langmuir was also higher that the R^2 (0.9483) of Freundlich, which implies the best fit in describing the adsorption of H_2S on the cocoa activated carbon. Moreover, the Langmuir model provided the q_m of 0.67 mg/mg (=670 mg/g) for TMA removal, and 0.2171 mg/mg (=217.1 mg/g) for H^2S removal were very close to the experimental $q_{e\ Exp}$ of 654.8 mg/g for TMA removal, and 220.37 mg/g for H_2S removal as show in the Table 3 which shows a good agreement with the adsorption capacity generated by Langmuir

isotherm model. On the other hand, Freundlich represented the n values (n=2.9735 for TMA removal; n=11.3122 for H_2S removal) were more than 1 (n=1), which indicated both of the adsorption of TMA and H_2S were physical (n>1). This is further validated by the isotherm linear data points show in the Fig. 7, showing a good agreement with the adsorption capacity obtained from the Langmuir and Freundlich isotherm models.

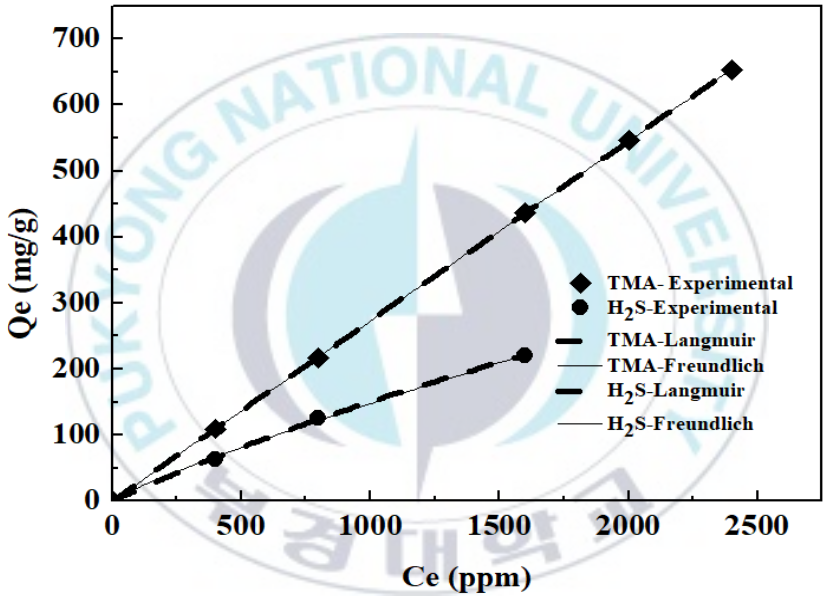


Fig. 7. Isotherm data points of TMA and H_2S adsorption using cocoa activated carbon.

3.4 Adsorption kinetic studies. [28]

Adsorption kinetics is an essential study for process design, it can contribute to determine the optimum operating condition, adsorbate uptake rate, and equilibrium time [26], which are aimed at increasing efficiency of the adsorption process. The experimental data were analyzed using the representative kinetic models of pseudo-first order for Eq. (4), pseudo-second order for Eq. (5), and intraparticle diffusion model for Eq. (6), respecticely.

$$log(q_e - q_t) = log q_e - \frac{k_1}{2.303} \cdot t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \quad (5)$$

$$q_t = k_i t^{0.5} + c_i \quad (6)$$

where q_e (mg/g): equilibrium adsorption capacity

q_t (mg/g): adsorption capacity at time, t (min)

$k_{1,\ 2,\ \text{and}\ i}$: rate constant of pseudo-first order

C_i: the thickness of the boundary layer

k1 (min^{-1}) k_2 (g/mg-min) k_i ($mg/g\text{-}min^{1/2}$)

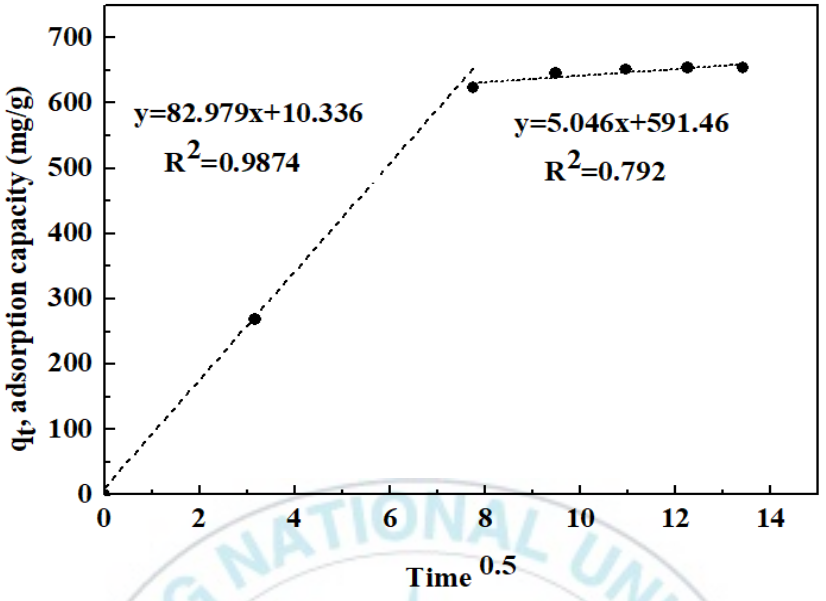
Table 3. Kinetic parameter constants and correlation coefficients.

Kinetic model		TMA		H_2S	
	parameter	value	R^2	value	R^2
Experimental	$q_{e.\ Exp}$	654.8	--	220.37	--
Pseudo-first order	k_1	0.0488	0.9991	9.672E-03	0.9983
	$q_{e.\ Theo}$	629.2		231.206	
Pseudo-second order	k_2	3.65E-03	0.9994	2.38E-04	0.9754
	$q_{e.\ theo}$	625		217.3913	
Intraparticle diffusion	k_{id-1}	82.979	0.9874	12.625	0.986
	c_{i-1}	10.336		-5.1413	
	k_{id-2}	5.046	0.792	3.564	0.9321
	c_{i-2}	591.46		146.41	
Yoon-Nelson	λ	6.1827	0.9449	58.612	0.9911
	k'	-0.0429		5.44E-03	

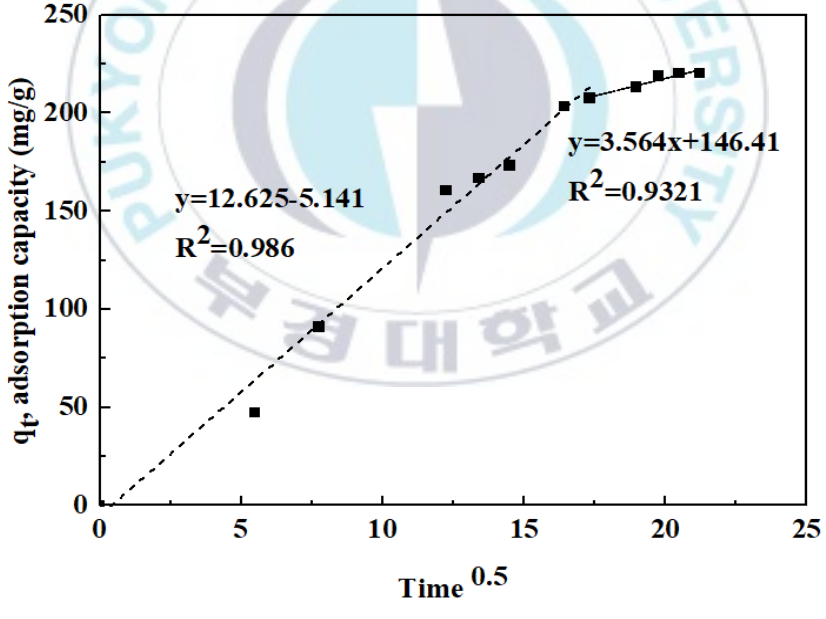
Table 3 shows the parameters and correlation coefficient values of different kinetic models. The experimentally obtained adsorption capacities were 654.8 mg/g for the TMA and 220.37 mg/g for the H_2S, which were compared to the theoretical adsorption capacity of each kinetic model. The TMA 654.8mg/g of experimental data is close to both of 629.2 mg/g of pseudo-first order and 625 mg/g of pseudo-second order, and H_2S 220.37 mg/g of experimental data is also between 231.206 mg/g of pseudo-first order and 217.3913 mg/g of pseudo-second order. Which indicated experimental values of TMA and H_2S is in agreement with the theoretical values generated by the pseudo-first order and pseudo-second order equation. Compared with

other studies such as adsorption capacity of TMA is in the range of 1.7 to 6.9 mg/g using activated carbon, biochar, and *S. Trifasciata* leaf powder [27,28]. Chung et al. [29] reported the maximum adsorption capacity was 87.7 mg/g for TMA removal with zeolite adsorption. And Lee et al. conducted TMA adsorption capacity was between 90 and 110 mg/g by modified activated carbon with acid or base [30]. For H_2S adsorption with activated carbon, the maximum adsorption capacity of sulfur was 72.4 mg/g generated by with MnO impregnated on activated carbon at 350 ^oC [31]. In addition, Mochizuki et al. [32] conducted H_2S adsorption was performed by the activated carbon from petroleum coke with KOH chemical activation. The adsorption capacity of H_2S was about 95 mg/g overall the adsorption process, which indicated that our study has a higher adsorption capacity than the current studies. Moreover, correlation coefficient values for pseudo-first order, pseudo-second order, intraparticle diffusion, and Yoon-Nelsom kinetic models were R^2=0.9991, R^2=0.9994, R^2=0.9796, R^2=0.9759, and R^2=0.9449 for TMA; were R^2=0.9983, R^2=0.9754, R^2=0.9862, R^2=0.9131, and R^2=0.9911 for H_2S, respectively. Among the kinetic models, the pseudo-second model showed the highest correlation coefficient for TMA (R^2=0.9994), and pseudo-first order provided the highest correlation coefficient for H_2S (R^2=0.9983) removals, followed by the intraparticle diffusion, Yoon-Nelson model. When it comes to the kinetic models, the coefficient $R^2$of TMA

adsorption was higher than the $R^2$of H_2S adsorption. This is because the kinetic model is better fit in describing the adsorption between the liquid and solid phases [33]. Although the TMA was adsorbated in the vapor phase during the experiment, TMA adsorption was much closer to adsorption between liquid and solid phases compared to H_2S adsorption of gas to solid. The intraparticle diffusion model is aimed at describing an adsorbate diffusion from the bulk of the solution into adsorbent micropores, it helps to offer a rate-limiting step [33]. Fig. 8 shows the intraparticle diffusion model plots, which initially represent a linear slope due to the bulk adsorbate diffusion and an equilibrated plateau later. The rate constants (k_{id-1}) of the adsorption in the linear region were higher (82.979 mg/(g-min)$^{1/2}$ for TMA and 12.625 mg/(g-min)$^{1/2}$ for H_2S than the rate constants (k_{id-2}) in the plateau region (5.046 mg/(g-min)$^{1/2}$ for TMA after 60 min and 5.0424 mg/(g-min)$^{1/2}$ for H_2S after360 min). because numerous empty micropores fraction distribute on the cocoa activated carbon, which has large intraparticle spaces where the bulk TMA adsorbates were rapid adsorbed during the initial few minutes. Once the micropores were fulfilled, the meso and macropores converted the interparticle space into a transport pathway for the adsorbed remaining pollutants showing the reduced rate constants (k_{id-2}).



(a)



(b)

Fig. 8. Intraparticle diffusion model plots for (a) TMA and (b) H_2S removals.

The Yoon-Nelsen model [34] was often applied to understand the relationship between the adsorption and transmission probability of gas molecules [35]. which fits better for a fixed bed adsorption study with porous sorbents, which includes both the adsorption of the adsorbates on an active site and the remaining adsorbates flowing through the pores. The equation of the Yoon-Nelsen model is given in Equation (7). That contributes to determine the two parameters of *k'* and λ.

$$t = \lambda + \frac{1}{k'} ln \frac{C}{C_i - C} \quad (7)$$

Where *t*, breakthrough time (min)

λ, 50% breakthrough time (min)

k', rate constant (1/min)

C_i, inlet concentration (mg/m3)

The Yoon-Nelson model was applied to analyze the TMA and H_2S adsorption when the pollution concentrations were 2400 ppm for TMA and 1600 ppm for H_2S. Though the goodness of fit wasn`t as high as the second order (for TMA), and the first order (for H_2S) kinetic models, a medium R^2 provided by Yoon-Nelsen model was 0.9449 for the TMA, and was 0.9911 for the H_2S, respectively. The high goodness of fit indicates the presence of both pollutant molecules

adsorbing on the carbon and the other flowing through the pores. The 50% breakthrough time (λ) was 6.1827 min for TMA adsorption and 58.612 min for H2S after the filter fan was started for adsorption at the initial pollution concentrations of 2400 ppm for TMA and 1600 ppm for H_2S.

3.5 Regeneration study of the used Cu/AC filter

The used Cu/AC filter for H_2S and TMA adsorptions were regenerated into air drying oven. The temperature was determined based on our previous work as show in Fig S1 [36], which shows the most derivative weight changes occurred under the significant peak around 200 ^oC. So, the 200 ^oC was chosen as regeneration temperature for the regeneration of the used Cu/AC filter. Fig. 9 shows the H_2S adsorption using the regeneration filter at varied regeneration residence time. The initial concentration of 400 ppm H_2S reduced to 200 ppm at 20 min with 10 min air dried regenerated filter. However, the initial concentration almost reduced to 0 ppm at 20min with 20 min air dried regenerated filter. In addition, the same regeneration and experiment method was employed for used TMA removal filter. However, no significant changes of TMA concentration were obtained with the regenerated filter.

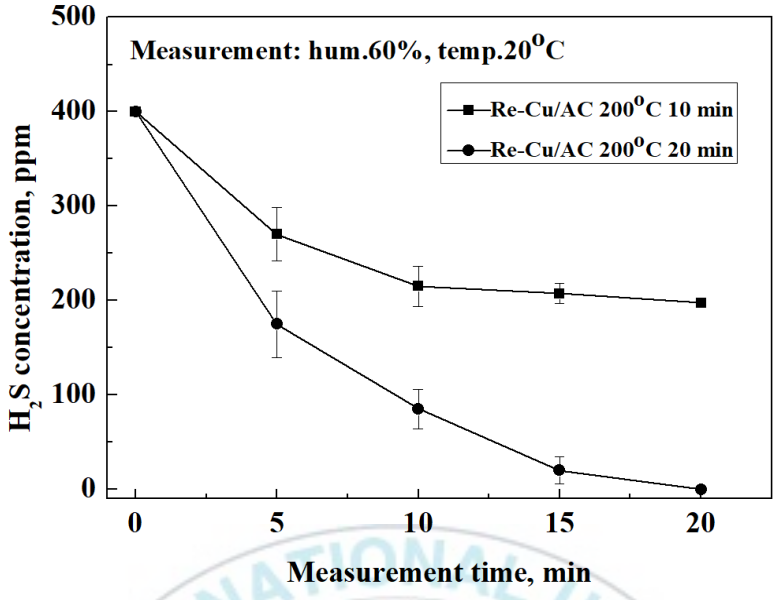


Fig. 9. H_2S removals with Cu/AC filter after air drying regeneration.

4. Conclusions

Cocoa activated carbon is a promising adsorbent for the adsorption of TMA and H_2S due to its high cost-effective, large surface area, numerous microporosity, as well as high adsorption capacity. The cocoa activated carbon (AC) and copper impregnated AC (Cu/AC) were evaluated for TMA and H_2S adsorptions for confined space use. The cocoa activated carbon with a copper catalyst represented the best toxic gas adsorption performance. Adsorption kinetic study showed that the pseudo-second order model and pseudo-first order model fitted best for the TMA adsorption and H_2S adsorptions, respectively. Moreover, both Lanmuir and Freundlich isotherm models showed the significance. The regenerated Cu/AC filter successfully re-adsorbed the H_2S gas. The study shows that cocoa activated carbon is a promising adsorbent for TMA and H_2S removal in confined space.

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