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The removal of low concentration formaldehyde over sewage sludge char treated using various methods

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Abstract−Sewage sludge char was activated, using several different methods, to be used for the adsorption of formaldehyde. First, sewage sludge was pyrolyzed at 700 °C for one hour to produce char. The sewage sludge char was then activated with 20% steam gas. To produce a chemically activated char, KOH was used with the char at a weight ratio of KOH/char=0.5. To produce another kind of activated char containing nitrogen functional groups, the sewage sludge char was activated with ammonia at 350 °C. These activated chars were used for indoor low concentration formaldehyde adsorption experiments. All the chars tested in this study were shown to have better performance than activated carbon. In particular, the char activated with both ammonia and KOH showed the best formaldehyde adsorption performance. This result was attributed to the combination of surface basicity due to large amounts of metal components and generation of oxygen and nitrogen functional groups as a result of the KOH and ammonia treatments.

Key words: Activated Sewage Sludge Char, Low Concentration Formaldehyde, Indoor Air

INTRODUCTION

Proceeding into the post industrial information era of the 21st century, the quality of human life is, to a large extent, improving both qualitatively and quantitatively. As people are spending more time indoors than before, indoor air quality has become one of the most important environmental concerns. With people spending sometimes more than 80% of their time indoors, they are exposed to various indoor air pollutants. In particular, sick house syndrome and multi chemical sensitivity due to indoor air pollution are drawing great attention [1,2].

Formaldehyde is a representative indoor air pollutant that is emitted through a variety of pathways, e.g., from tobacco, building interior decoration materials and furniture. In particular, formaldehyde is a well known carcinogen that induces gene toxicity, as well as paranasal sinus and nasal cavity cancer. In Korea, the formaldehyde concentration standard is designated as a short-term exposure limit of 1 ppm in the Enforcement Ordinance of the Industrial Safety and Health Act. A popular method for the removal of airborne formaldehyde is adsorption with carbonaceous adsorbent [3,4]. However, research on adsorbents which remove indoor formaldehyde from air remains insufficient. Song et al. [5] investigated low concentration formaldehyde removal using pitch-based, rayon-based, and PAN-based activated carbon fibers. They reported that the PAN-based activated carbon fiber gave the best adsorption performance for the removal of formaldehyde. Kumagai et al. [6] carried out a study on the adsorption of low concentration formaldehyde and acetaldehyde using rice husk char carbonized by heat treatment. In their experiments, the rice husk char showed better adsorption activity than granular coconut-shell activated carbon.

The continuous increase in sewage sludge production is also an important environmental concern. Most sewage sludge is disposed of via landfilling, ocean dumping and incineration, of which ocean dumping accounts for the largest portion. Only a small amount of sewage sludge is reused. As ocean dumping will be banned from February 2011, according to the London Convention, the development of a new on-land treatment method is urgently required. Much effort has been made to meet this requirement, particularly on thermal treatment methods, such as combustion, pyrolysis and gasification. In particular, fast pyrolysis is used to produce bio-oil from sewage sludge. During the fast pyrolysis of sludge, char is produced as a byproduct. If the biomass char can be used as a replacement for activated carbon [7], the economics of fast pyrolysis of sludge will be increased.

In this study, sewage sludge was pyrolyzed to produce char, which was then used for the adsorption of low concentration (1 ppm) formaldehyde. Several different pre-treatment methods were applied to improve the formaldehyde adsorption performance of the char.

EXPERIMENTAL

1. Sewage Sludge

The sewage sludge was collected at J sewage disposal plant, and

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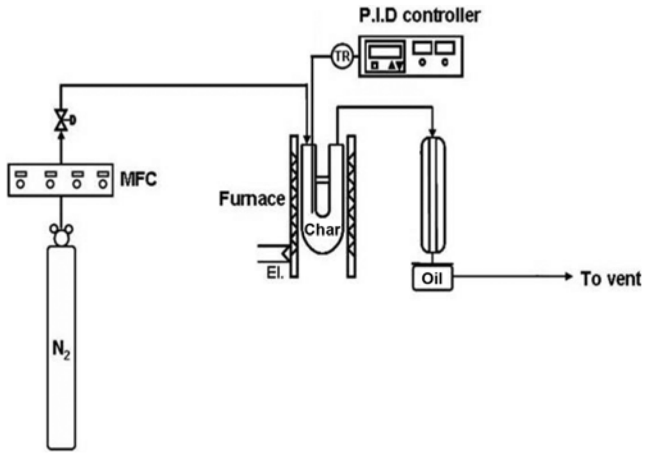

Fig. 1. Schematic diagram of sewage sludge pyrolysis apparatus.

dried and sieved with a 150-200 mesh. Char was produced via fast pyrolysis at 700 °C for one hour under a N_2 flow of 50 ml/min. The char produced in this way will be hereafter referred to as SC. Fig. 1 shows a schematic of the apparatus used for producing the sewage sludge char in this study.

2. Methods of Char Activation

The char produced via pyrolysis was treated with steam, KOH and/or ammonia to modify its property.

In the steam treatment, the char was placed in the reactor, and then purged with a gaseous mixture of 80% N_2 and 20% H_2O at a flow rate of 50 ml/min. The reactor temperature was raised from room temperature to 700 °C at 5 °C/min, using a PID, and maintained at 700 °C for one hour to activate the char (Fig. 2). The char treated in this way will be hereafter referred to as SCW.

KOH treatment has been reported as a good way to treat activated carbon [7]. A KOH and char mixture, with the weight ratio of KOH/char=0.5, was dried on a hot plate for two hours to evaporate any moisture and then further dried at 110 °C in an oven for 24 hours. The dried samples were pulverized before being placed into the reactor. The reactor was purged with N_2 gas at a flow rate of 50 ml/min. The reactor temperature was raised from room temperature to 700 °C at 5 °C/min and maintained at 700 °C for one hour. The samples were neutralized with 5-M HCl to remove any K^+ ions

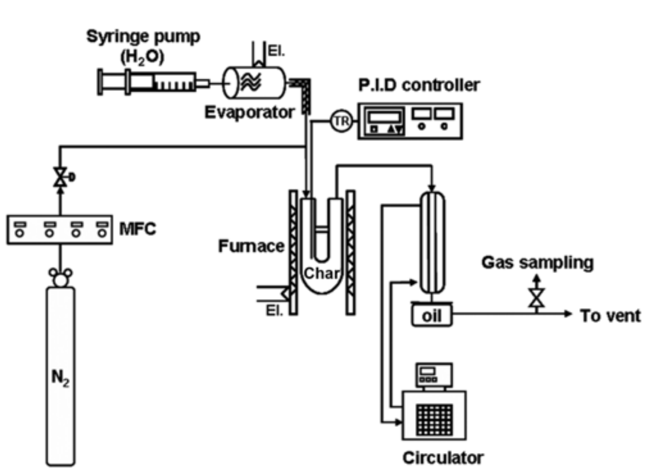

Fig. 2. Schematic diagram of physical activation apparatus.

remaining before being washed with distilled water and then dried. The char treated in this way will be referred to as SCK.

In ammonia treatment, the sewage sludge char was placed into the reactor and treated at 350 °C for two hours, under an ammonia gas flow of 50 ml/min. The ammonia adsorbed onto the char surface was then removed by nitrogen purging at a flow rate of 50 ml/min for another one hour. The char treated in this way will be referred to as SCA. SCK was also treated by ammonia and it will be referred to as SCK+SCA.

Commercial activated carbon (DDG-480) for gas phase was purchased from Kaya Activated Carbon Inc.

3. Characterization of Sludge Char

FT-IR was used to qualitatively analyze the chemical functional groups on the samples. To characterize the oxygen (-COOH, -OH, -COO, -C=O, etc.) and nitrogen functional groups, the FT-IR measurement of the char surface was carried out from 4,000 to 400 cm^{-1}.

An elemental analyzer (Flash EA 1112 Series, CE Instruments/Thermo Quest Italia) was used to analyze the C, H, N and S in the samples at 1,100 °C. An analysis of O was then conducted at 1,060 °C under reducing condition.

Analyses of the metal components in the samples were performed using an ICP-AES (Inductively Coupled Plasma Emission Spectrometer, Optima-4300, Perkin Elmer).

To measure the BET specific surface area, pore volume and pore size distribution of the produced chars, a nitrogen adsorption/desorption analysis (BELSORP-MINI, BEL Japan Inc.) was conducted at 77 K for the samples pre-treated under vacuum at 200 °C.

A pyrolysis test of the sewage sludge was performed using a TGA analyzer (PerkinElmer, Pyris 1 TGA). A typical sample mass of 10 mg was heated at 10 K/min, with nitrogen purging, to a final temperature of 900 °C.

4. Adsorption of Formaldehyde over Sludge Char

The adsorption experiment was performed by using the method described in literature [8]. The 100-ppm formaldehyde produced by Union Inc. was used in this study. A 10-L aluminum bag (for preventing oxidation by sunlight) was cleaned using N_2 gas and then emptied with a vacuum pump. Formaldehyde was injected into the bag, with N_2 gas then added to adjust the formaldehyde concentration at 1 ppm. Then, 0.07 g of the activated char was put into the aluminum bag containing 1-ppm formaldehyde. The char was dried at 100 °C in an oven for 24 hours to remove the influence of moisture. During the adsorption process, the temperature was controlled at 20 °C using an incubator to avoid any temperature dependency [8]. Sample bags were agitated in a shaking incubator for enhancing the gas-solid mixing.

The amount of formaldehyde adsorbed was measured with a formaldehyde analyzer (4000Series, Woori System, Korea), with measurements made at 10, 30, 50 and 70 min.

RESULTS AND DISCUSSION

1. Sewage Sludge

Table 1 shows the results of the ultimate and elemental analyses of the dried sewage sludge. The results of the metal component analyses of the dried sewage sludge are shown in Table 2. O and N are expected to form oxygen and nitrogen functional groups, respectively, on the char surface during its production and activation, which

Table 1. Proximate and ultimate analyses of dried sewage sludge

Proximate analysis (wt%)	Moisture	5.2
	Volatile matter	46.2
	Fixed carbon	10.0
	Ash	38.6
Ultimate analysis (wt%)	C	39.7
	H	6.1
	O	47.5
	N	5.5
	S	1.2

Table 2. Elemental analysis of dried sewage sludge (unit: ppm)

Element	Concentration
Si	56
Al	26855
Ca	25030
Fe	10780
K	3857
Mg	6630
Na	860
Zn	1546
P	17405

would enhance the adsorption performance [6,8]. Compared to other biomass, sewage sludge contains large amounts of ash stemming from earth and organic materials. The metal components, such as Na, Fe, Ca, Al, K, Ti, Zn and Mg, were also high. In particular, base metals, such as Ca, K and Mg, have been reported to enhance the formaldehyde adsorption performance [6,9]. Therefore, inclusion of such metal components was expected to be advantageous in the adsorption of formaldehyde by the chars.

Fig. 3 shows the results of the TGA analysis of the dried sewage sludge. The weight began to decrease rapidly at about 250 °C, but then gradually slowed down and reached almost 50% of initial weight above 600 °C, at which point all the gaseous and liquid components had been removed, leaving only solid components with large specific surface areas and porous structures, which would be

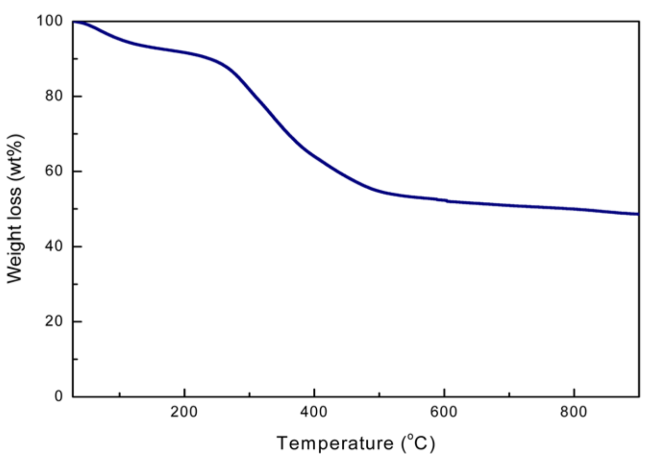

Fig. 3. TGA of dried sludge.

Table 3. Elemental analysis of sewage sludge chars treated using various methods (unit: ppm)

Element	SC	SCW	SCK
Al	94170	80200	51210
Ca	48840	41230	3158
Fe	38250	33350	12360
K	16720	16520	25730
Mg	11010	10810	1804
Na	9417	9299	5679
Zn	2701	2553	405
P	33600	32380	1783

expected to be favorable for adsorption. Therefore, sewage sludge was pyrolyzed at 700 °C to make chars.

2. Characterization of Sludge Char

Table 3 shows the metal content of the produced chars. The untreated char, SC, and the steam-treated char, SCW, were observed to have similar contents of most metal components. However, the KOH-treated char, SCK, lost a considerable amount of its metal components during the treatment. The contents of the base metals, Ca, K and Mg, which are known to enhance the formaldehyde adsorption performance, were observed to be high in both the SC and SCW [7].

Fig. 4 shows the FT-IR spectra obtained to identify the functional groups developed on the surfaces of the sewage sludge chars activated by the different methods. The intensity of the C-O stretching vibration peak appearing at 1,200-1,300 cm^{-1} was shown to be increased by activation. The intensity of the hydroxyl O-H stretching peak around 3,600 cm^{-1} was also shown to be increased by activation. In addition, the intensities of the C=O stretching peak (1,600 cm^{-1}) and peak of NH group (1,650 cm^{-1}) were also shown to be increased by KOH and NH_3 activation, respectively. The increased peak intensities were dependent on the activation method. In particular, the peak intensity at 1,650 cm^{-1} was increased when the char was treated with both KOH and ammonia (SCK+SCA), which was attributed to the growth of the C=O peak as a result of the KOH treatment and the growth of the nitrogen functional group peak as

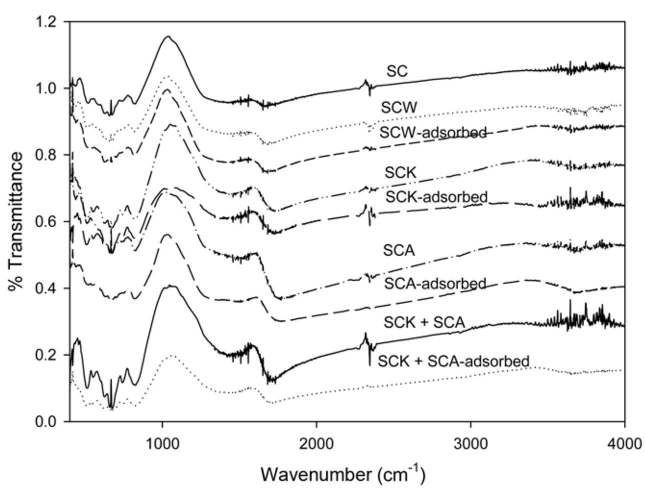

Fig. 4. FT-IR spectra of chars treated using various methods.

Table 4. Physical properties of chars and activated carbon

Sample name	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Ave. pore diameter (nm)
SC	47	0.04	3.7
SCW	64	0.06	3.8
SCK	434	0.35	4.3
SCA	42	0.04	3.6
SCK+SCA	371	0.31	4.2
Activated carbon	400	0.30	1.8

a result of the ammonia treatment.

Various functional groups, including, in particular, those of oxygen and nitrogen, are known to affect the formaldehyde adsorption performance [4-6,8,10]. Fig. 4 also shows that the peak intensities around 1,200-1,300, 3,600 cm^{-1} (SCK) and 1,650 cm^{-1} (SCA and SCK+SCA) were reduced after formaldehyde adsorption. This implies that formaldehyde adsorbed on oxygen and nitrogen functional groups. Table 4 shows the results of the BET analyses for each char. The SC, produced at 700 °C, had the specific surface area at 47 m^2/g. When this char was treated with steam, the specific surface area increased to 64 m^2/g; whereas, when it was treated with KOH, the specific surface area jumped dramatically to 434 m^2/g. This huge surface area increase may be due to the consumption of ashes by the KOH treatment. Assuming that only the carbonaceous part of the material provides surface area, increase of carbon surface area is readily explained by the opening and development of the porosity, due to simultaneous activation and elimination of ashes. Fierro et al. reported a similar result [11]. However, when SC and SCK were treated by ammonia, the surface areas of chars (SCA and SCK+SCA) decreased due to probably pore blocking of ammonia. These results demonstrated that the physical and chemical treatments had contributed to increasing not only the amount of functional groups, but also the specific surface area. In addition, the ash content decreased significantly for KOH treatment, while steam and ammonia treatments did not affect the ash contents (Table 5). This implies again that for SCK, SCA and SCK+SCA, the surface functional groups due to oxygen and nitrogen may have played a major role for formaldehyde removal.

3. Adsorption of Formaldehyde over Sludge Char

Fig. 5 shows the results of the formaldehyde adsorption experiments using SC, SCW, SCK and SCA. The fastest adsorption took place during the first 10 minutes, and then gradually decreased. In 50 minutes, the adsorption rates of most chars become very low, as the adsorption with some chars is often complete. The adsorption performance of the chars was compared to that of a reference material, activated carbon, to evaluate the relative performances of the chars. All the chars tested in this study showed better performance than activated carbon in formaldehyde adsorption. Although sewage sludge char has a small surface area, the large amounts of base

Table 5. Ash contents in chars

Sample name	SC	SCW	SCK	SCA	SCK+SCA
Ash content (wt%)	75.0	74.0	39.0	75.3	39.4

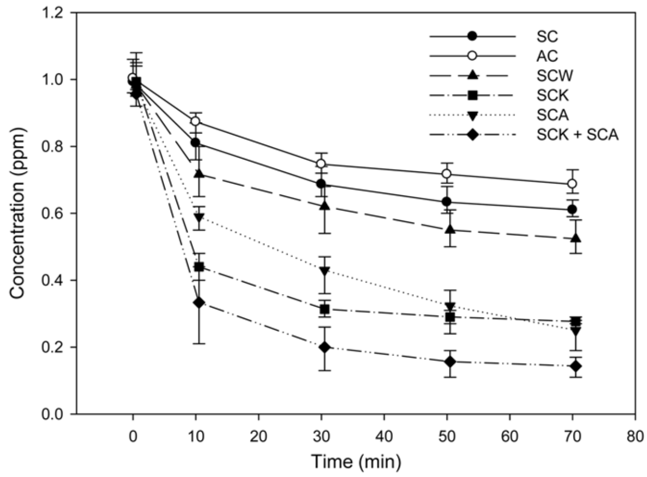

Fig. 5. Adsorption of formaldehyde over chars treated using various methods.

metals contained in the char are thought to promote the adsorption of formaldehyde. In addition, as shown in Table 4, the average pore size of activated carbon was smallest but the ability of formaldehyde removal was lowest. This may indicate that pore size was not the dominant factor for removal of formaldehyde in this study. Kumagai et al. [6] suggested that Ca and K increased the surface alkalinity, resulting in enhanced formaldehyde adsorption. Also, Busca et al. [9] studied the role of basic sites in the adsorption and transformation of formaldehyde on inorganic oxides using FTIR spectroscopy. They confirmed that basic sites, such as MgO, could polymerize formaldehyde to $(-CH_2O-)_n$, leading to transformations into methoxy groups and formate ions.

Steam-treated chars (SCW) had larger specific surface areas (Table 3) and contained larger amounts of functional groups (Fig. 4) than SC. The metal content was little affected by steam-treatment. Therefore, the increased activity of SCW was thought to be due to the increased amount of oxygen functional groups. In the case of the KOH-treated char (SCK), which showed the largest surface area and contained the largest amount of oxygen functional groups, the formaldehyde adsorption activity was also shown to be the highest. As shown in Fig. 4, the peak intensities of SCK and SCW around 1,200-1,300 cm^{-1} and 3,600 cm^{-1} were reduced after formaldehyde adsorption. Rong et al. [3] and Boonamnuayvitaya et al. [12] also reported that surface hydrophilic and polarized oxygen-containing functional groups, as well as large specific surface areas and pore volumes, enhanced formaldehyde adsorption onto coffee residue-based activated carbons and oxidized Rayon-based activated carbon fibers, respectively. Dipole interactions and hydrogen bonding between formaldehyde and oxygen-containing functional groups were responsible for the increased formaldehyde uptake. El-Sayed and Bandosz [13] showed that surface oxygen-containing functional groups interacted strongly with acetaldehyde, resulting in increased acetaldehyde uptake.

The enhanced activity of ammonia-treated char (SCA) can be attributed to the generation of nitrogen functional groups during the treatment. As is shown in the FT-IR result of Fig. 4, the ammonia treatment considerably increased the amount of nitrogen functional groups, which was thought to have enhanced the adsorption activity. Obviously, the peak intensity of nitrogen functional group around 1,650 cm^{-1} was reduced greatly after formaldehyde adsorption. Some studies have reported that increased amount of nitrogen functional groups improves the formaldehyde adsorption performance. Tanada et al. [4] introduced nitro groups onto the surface of activated carbon using nitric acid treatment. The amount of formaldehyde adsorbed onto this activated carbon increased with increasing degree of ammoxidation of the activated carbon due to the increased interaction between the surface of the activated carbon and formaldehyde. Kim et al. [8] investigated the effects of introduction of various amine groups to mesoporous materials, and reported increased formaldehyde adsorption performance with increasing amount of amine groups introduced. They argued that the interaction between amine groups and formaldehyde contributed to the enhanced adsorption.

Inspired by the above results, we treated the char initially with KOH and then additionally with ammonia to introduce large amounts of both oxygen and nitrogen functional groups (SCK+SCA). The formaldehyde adsorption experiment confirmed that SCK+SCA had the best performance of all the chars tested in this study. Also, the peak intensities of both oxygen and nitrogen functional groups decreased greatly after formaldehyde removal.

CONCLUSIONS

We investigated the feasibility of producing an alternative adsorbent by activating sewage sludge char that could be used as a replacement for activated carbon. The sewage sludge char showed better formaldehyde adsorption performance than activated carbon, even without any treatment, which was attributed to the surface basicity by large amounts of metal components contained within the char. When the sewage sludge char was treated with steam, KOH and ammonia, the amounts of oxygen and nitrogen functional groups, as well as the specific surface area of the char increased, depending on the treatment method, and resulted in improved formaldehyde adsorption performance. In particular, the KOH treatment increased the amount of oxygen functional groups, while the amount of nitrogen functional groups was increased by the ammonia treatment. However, the char activated with both KOH and ammonia gave the best formaldehyde adsorption performance. In summary, the combination of the surface basicity due to metal components and oxygen and nitrogen functional groups was beneficial for formaldehyde adsorption.

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