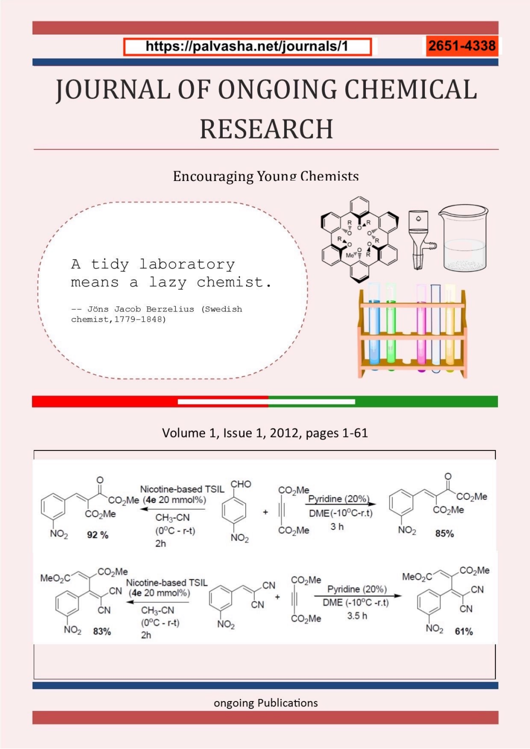
COMPARISON OF ETHYLENE ADSORPTION ONTO ACTIVATED CARBON CLOTH AND GRANULATED ACTIVATED CARBON IN DYNAMIC PHASE



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A tidy laboratory means a lazy chemist.

-- Jöns Jacob Berzelius (Swedish chemist,1779-1848)

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Research Article

Comparison Of Ethylene Adsorption Onto Activated Carbon Cloth And Granulated Activated Carbon In Dynamic Phase

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Abstract

In this study, ethylene gas adsorption onto activated carbon cloth (ACC) and granulated activated carbon (GAC) were compared in dynamic phase using a home-built apparatus. ACC or GAC were placed into filter holder and a constant concentration of ethylene gas was introduced throughout AC filter at a constant flow. From the gas flow just after the AC filter a certain amount of gas was taken by an injector and analyzed using gas chromatography to determine the amount of decrease in ethylene gas concentration. It was found that ethylene gas adsorption capacity of ACC was 8.33 fold greater than that of GAC.

Keywords: Activated Carbon Cloth, Adsorption, Volatile Organic Compounds, Ethylene, Activated Carbon

INTRODUCTION

It is reported that the long-term exposure to volatile organic compounds (VOCs) causes health defects such as eye and throat irritation, allergies, damage on the liver and central nervous system, etc. [Ruddy et al, 1993;Emamipour et al, 2007;Mallouk et al, 2010;Johnsen et al, 2011;Das et al, 2004]. Due to these health effects of VOCs, it is important to remove them from indoor and outdoor air. There are various methods to remove VOCs such as condensation, adsorption, catalytic oxidation and thermal oxidation [Ruddy et al, 1993;Emamipour et al, 2007;Mallouk et al, 2010;Johnsen et al, 2011;Das et al, 2004;Rafson, 1998]. Ruddy and Carrol (1) have summarized the comparative performances of these techniques regarding their advantages, limitations and operating costs. The authors termed “adsorption” as the “state-of-art” technology has immense potential for VOC control. The materials that are used to remove VOCs by adsorption are metal-organic frameworks (MOFs) [Yang et al, 2013;Zhao et al, 2011], TiO_2–SiO_2 pellets [Zou et al, 2006], zeolites [Zhou et al, 2014] and activated carbon [Chuang et al, 2003;Ramos et al, 2010;Fuertes et al, 2003] etc. but among them activated carbon is the most effective and most frequently used adsorbent to remove especially low concentration of VOCs [Bashkova et al, 2005;Bhargavi et al, 2011;Devai et al, 1999;Dwivedi et al, 2004;RomeroAnaya et al, 2014]. The adsorption capacity of activated carbon is directly based on its specific surface area, pore size and pore size distribution and surface chemistry. Although there are three types of activated carbon (powdered, granulated and fiber/cloth), the most commonly used type is the granulated form. But the fiber/cloth form has gained increasing attention in recent years due to its several advantages over GAC such as higher dynamic adsorption capacity and adsorption rate, a higher value of the surface area, more homogeneous micropore size distribution and smaller critical bed depth [Bansal et al, 2005]. There are many studies using ACC in the removal of VOCs in the literature [Ramos et al, 2010;Singh et al, 2002;Fournel et al, 2005;Cal et al, 1996;Cal et al, 1997;Huang et al, 1999]. Singh et al. (2002) have used ACC as an adsorbent for the removal of benzene and n-hexane from the single component and mixture systems. They reported that adsorption of n-hexane onto ACC was found to be more favorable in comparison to benzene. In another work, Huang et al, 1999 have studied the adsorption behavior of VOCs onto a packed bed of three types of ACC. They concluded that the higher the BET surface area of ACC, the higher would be the adsorption capacity. Besides, there are some comparative studies for granulated and cloth form of activated carbon. For example, Brasquet et al, 1997 compared ACC and GAC for their adsorption efficiency in wastewater and air treatments. They concluded that the adsorption rate of ACC was 5-10 folds higher than GAC [Brasquet et al, 1997]. By referring some studies [Abe et al, 1992;Suzuki, 1991] they also concluded the increase in the rate of adsorption was resulted from micropores being directly on the external surface fiber and narrow size distribution around 2.5 to 2.6 nm [Ko et al, 1992]. In addition, Balanay et al. studied comparison of adsorption of toluene onto GAC and different type of ACCs and they reported that ACC with BET surface area of 1.500 $m^2.g^{-1}$ has better performance (28%) than GAC with BET surface area of 1.500 $m^2.g^{-1}$ [Balanay et al, 2011]. In another interesting study, Fournel et al. (2005) compared the performance of two kinds of activated carbon fiber (ACF) adsorbents (cloth and felt) to remove VOCs (a single component of toluene, ethyl acetate, methylethylketone, dichloromethane, isopropanol, and acetone) from polluted air. They showed that for all VOCs studied ACC has higher adsorption capacity than activated carbon felt.

Ethylene is ripening hormone which is released by fruits, vegetables, and flowers during post-harvest storage. Depending on the concentration of ethylene releasing from stuff and entering from the environment, ethylene accelerates ripening which causes premature aging and rotting of fruits and vegetables. The decaying of fruits and vegetables can be slowed by refrigeration and humidity control but they are not enough to stop the production of ethylene. In many refrigerators activated carbon filter is used to adsorb ethylene gas by cycling the air in it.

The main purpose of this work is to study and compare the dynamic phase ethylene gas adsorption capacities of ACC and GAC. A commercial GAC used in refrigerators and newly patented ACC were used in the experiments.

RESULTS AND DISCUSSION

Characteristics of ACC and GAC

The specific surface area of GAC was calculated according to Brunauer, Emmet, Teller (BET) method using the linear part of the nitrogen adsorption isotherm. The characterization of ACC and some of those results are given in Table 1. As seen from the data in Table 1, while S_{BET} of GAC with the total micropore area of 464 $m^2.g^{-1}$ is 894 $m^2.g^{-1}$, S_{BET} of ACC with the total micropore area of 468 $m^2.g^{-1}$ is 518 $m^2.g^{-1}$. Although ACC has lower S_{BET} value than GAC, their micropore areas are almost the same.

As in S_{BET} results pH_{pzc} value of GAC (7.0) almost same the pH_{pzc} value of ACC (6.8). On the other hand, the result of the surface functional groups analysis as shown that the total acidic group of ACC (3.8 meq/g) approximately 2 times more than that of GAC (2.0 meq/g). In addition, total basic groups of ACC (4.1 meq/g) is more than twice the total basic groups of GAC (1.7 meq/g). While the lactonic groups of ACC and GAC are almost equal (0.4 and 0.6 meq/g respectively), the phenolic groups of ACC (1.4 meq/g) are more than twice phenolic groups of GAC (0.6 meq/g). Besides, ACC has two times more carboxylic groups than GAC (2.0 and 0.8 meq/g). So, the total number of functional groups on the surface of ACC is much higher than that of GAC.

Table 1. Physical properties of the ACC and GAC

Sample	BET surface area ($m^2.g^{-1}$)	Micropore area ($m^2.g^{-1}$)	pH_{pzc}	Surface functional groups (meq/g)				
				Total acidic groups	Total basic groups	Carboxylic groups	Lactonic groups	Phenolic groups
ACC	518,0	468,0	6,8	3,8	4,1	2,0	0,4	1,4
GAC	894,0	464,0	7,0	2,0	1,7	0,8	0,6	0,6

Adsorption of Ethylene on ACC and GAC

In the dynamic phase adsorption comparison between ACC and GAC studies, ethylene gas concentration and flow rate was fixed at 12.5 ppm and 4.0 LPM respectively. Under these conditions, the adsorption capacities of ACC and GAC filters for one cycle were calculated according to the following equation;

$$\%Reduction = \frac{(Ci - Cf) \times 100}{Ci} ....eq.1$$

where C_i is the initial concentration of ethylene in ppm and C_f is the final concentration of ethylene in ppm after passing through filter. The percentage reduction of ethylene with ACC and GAC filters are given in Table 2.

Table 2. The concentration of ethylene detected by GC-MS

Sample	The initial concentration of ethylene (ppm)	The final concentration of ethylene (ppm)	The amount of ethylene reduction (%)
Without filter	12.5	12.5	0
ACC filter	12.5	7.5	40.0
GAC filter	12.5	11.9	4.8

As seen in Table 2, ACC decreases the concentration of ethylene by 40% under conditions studied for one cycle while decrease for GAC is 4.8%. In the experiments, ten layered ACC (0.8242 g) and GAC (2.2166 g) were placed to fill out the filter holder. Although the amount of GAC in the filter holder was much higher, its removal efficiency for ethylene was much lower than that of ACC. When relative adsorption capacities for ACC and GAC were calculated, ethylene adsorption onto ACC and GAC was found to be 6.1 ppm/g of ACC and 0.3 ppm/g of GAC, respectively. Also, relative adsorption capacity of ethylene onto ACC was found to be 20.3 fold higher than that of GAC. It is well known that the rate of adsorption in both static and dynamic phases is influenced by surface chemistry, particle size, pore size distribution, and the number of accessible micropores of the adsorbent. As mentioned above the surface chemistry of ACC which increases adsorbate-adsorbent structural interactions is much developed which explains its increased adsorption capacity for ethylene regarding surface chemistry of GAC studied under the same conditions. Furthermore, GAC studied has the particles of 10.1 µm average diameter and ACC have the fibers of an average diameter of 5.5 µm. The observed higher adsorption capacity of ACC may also come from its filamentous structure having micropores directly on the external surface. So, the adsorption sites in the micropores on the surface of fiber are easily accessible for adsorbates without additional diffusion resistance of macropores which usually is the rate-controlling step in the case of granular adsorbents. While both microporous areas of ACC and GAC are almost same GAC has 530 m^2/g, ACC has 50 m^2/g of mesoporous or microporous area respectively. Another parameter that results in lower adsorption for GAC is the larger space between GAC particles resulting from their larger diameter, which decreases contact surface area for ethylene gas flowing throughout filter.

EXPERIMENTAL

Materials

ACC was provided by Nume Kimya (Antalya, Turkey) coded as GDSEL 651. GAC was provided by Vestel (Turkey). Ethylene gas (99 % pure) was obtained from Lindegaz. Ethylene gas concentration was determined by gas chromatography (Finnigan Trace GC Ultra, Thermo Electron S.p.A. Strada Rivoltana 20900 Radano).

Characterization of GAC

The surface area of GAC was measured by nitrogen adsorption using a Quantachrome Autosorb-1-C/MS apparatus in relative pressure ranging from 10^{-6} to 1. Before measurement, GAC sample was degassed at 130 °C under vacuum (up to 10^{-6} torr) for 12 h. The BET specific surface area, S_{BET}, of GAC was calculated by using the software of the apparatus.

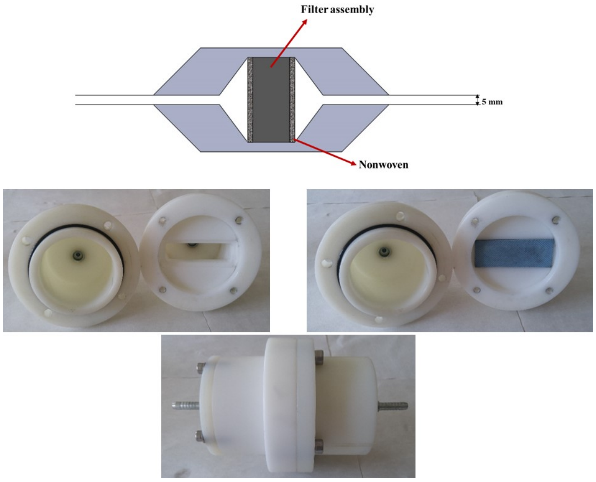

Figure 1. The schematic diagram and pictures of house- built filter apparatus

The pH_{pzc} value of GAC was determined using batch equilibrium method developed by Babic et al [Babic et al, 1999]. A certain amount of GAC samples were placed into an Erlenmeyer flasks and 20 ml of 0.01 M NaNO3 were added. The sample solutions' pHs were adjusted to different pHs by adding NaOH or HNO_3 solutions, then they were shaken for 24 h. At the end of contract period, the H^+ and OH^- ion concentrations were measured with the pH meter. Then the amounts of OH^- and H^+ ions adsorbed were calculated by subtracting the last measured concentrations of H^+ and OH^- ions from the initial concentrations calculated from initial and final pHs. The pH_{pzc} value of GAC was determined as the pH where the difference between the initial and the final H^+ or OH^- ion concentration is zero.

Boehm method [Boehm, 2002] was used to determine the surface functional groups of GAC studied. 0.05 g of samples of GAC was placed into acidic and basic solutions which were previously prepared using HCl, NaOH, Na_2CO_3, and $NaHCO_3$. Solutions were shaken for 48 h to make sure that equilibrium was established between GAC surface and acids or bases. After filtration, 20 ml samples were titrated against 0.1 M HCl or 0.1 M NaOH depending on whether the acidic or basic functional groups were determined. In Boehm titration, it is assumed that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na_2CO_3 neutralizes carboxylic and phenolic groups, $NaHCO_3$ only neutralizes carboxylic groups.

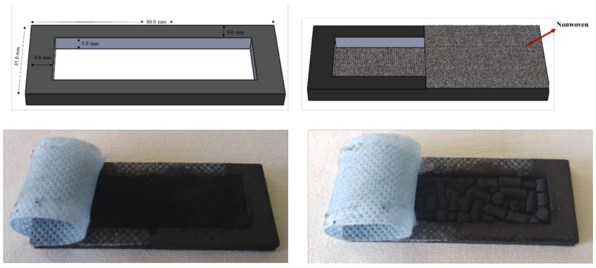

Figure 2. A schematic diagram and pictures of ACC and GAC filter holder

Adsorption test

A specially home-built filter apparatus was used to carry out the adsorption experiments. The diagram of the home built filter apparatus is shown in Fig. 1. 2. A holder was used to keep GAC and ACC samples where air flow passes through in as shown in Fig.2. The samples (GAC and ACC) were sandwiched in the rectangular hole of the filter holder using permeable nonwoven glued on the sidebands. For experiments, ten layered ACC (0.8242 g) and GAC (2.2166 g) were placed into the filter holder. Then the filter holder was inserted into filter apparatus and clinched using gasket and screw to prevent any gas leakage. Ethylene gas tank was connected to the air diluting system, filter apparatus, flow meter, and vacuum pump respectively as shown in Fig. 3.

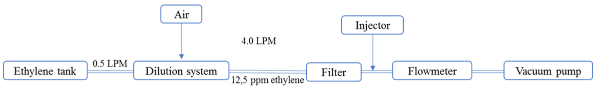

Figure 3. A schematic diagram of experimental system

While the system was running, 10 µL ethylene-air mixture was taken using a gas-tight syringe from flow between flow meter and filter apparatus and it was injected into the gas chromatograph equipped with Flame Ionization Detector (FID). For all experiments, gas mixture was intaken from flow just 1 min later running the pump. The GC was earlier calibrated with standard ethylene. The detection of the ethylene was achieved by a GC system (Finnigan TraceGC Ultra, Thermo Electron S.p.A. Strada Rivoltana 20900 Radano) equipped with an 80/100 alumina f-1 (1 m * 4.7625 mm *3,7 mm) column. Chromatographic conditions are as given below: oven temperature: 90 °C, analysis time: 2 mins, inlet: 200 ml.min^{-1}, pressure: 21.322 psi, total flow: 25 ml.min^{-1}, detector temperature: 170 °C, hydrogen flow: 35 ml min^{-1}, dry air flow: 350 ml.min^{-1}. The experiments were repeated three times for all ACC and GAC filters.

CONCLUSION

Although ACC has BET surface area of 518 m^2.g^{-1}, it reduces the ethylene gas concentration by 8.33 fold compared to that of GAC having BET surface area of 894 m^2.g^{-1}. Also, micropore areas and pH$_{pzc}$s of ACC and GAC are almost same. Therefore, based on the results obtained, it can be concluded that adsorption of ethylene onto activated carbons is directly related to chemical structure (functional groups) and the number of accessible micropores on the external surface of the activated carbons studied. Another reason for relatively lower adsorption for GAC is the larger space between GAC particles resulting from their larger diameter, which decrease contact surface area for ethylene gas flowing through the filter. It should be noted that ACC currently commands a higher price than the GAC, but its adsorption efficiency is much higher as clearly demonstrated from the data in this work. So, cost and performance balance should be considered when choosing the adsorption media for desired application areas.

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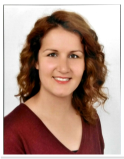

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