Adsorption of Volatile Organic Compound (VOCs) Over Formulated Prechar

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Abstract. Volatile organic compounds (VOCs) are being released as a result from incomplete combustion processes in the industry. Dry sorbent injection of activated carbon on fabric filters is one of the methods that are being used for VOCs removal in the flue gas. Dry sorbents act as filter aids to enhance the adsorption efficiency besides to overcome wear and tear problems that occurred during filtration. Biochar which is grinded bamboo charcoal was combined with PreKot™, a pre-coating agent as a filter aids formulation. This study introduced a newly two filter aids formulation known as PreChar10:90 and PreChar20:80 besides biochar as raw material. These three samples were initially evaluated through physical properties of moisture content and surface area before being tested on adsorption tests. PreChar20:80 and biochar presented a good sign with lower moisture content 3.306% and 3.417% respectively. Besides, surface area of both PreChar formulations was consecutively low compared to biochar due to PreKot™ existence as the PreKot™’s size is much larger. Large particle size of the filter aids results in low surface area available. In the adsorption test, flow rates were manipulated to be 0.1 L/min, 0.3 L/min and 0.5 L/min during the adsorption process. Filter aids formulation promises a huge amount of adsorption capacity by having longer period breakthrough points at which filter aids start to be saturated. It can be concluded that PreChar20:80 results in the highest adsorption capacity at all three different flow rates with 0.437 mg/g, 2.353 mg/g and 11.031 mg/g respectively. In this regard, PreChar20:80 has the potential to be an alternative material for activated carbon in the fabric filter application.

1. Introduction

VOC presence in the gas emission is due to an incomplete oxidation during incineration of municipal solid waste [1]. General VOCs such as chlorinated molecules, aromatics or oxygenated products are found in flue gas at relatively low concentrations. Gas streams that contain VOC will be treated using activated carbon that attaches to the fabric filter during the filtration process. Fabrics filters have become high demand among the popular options for particulate matter removal from gas streams as air
pollution control technology, but it seems sensitive towards high temperature and humidity. Fabrics filter formed in cylindrical or envelope bags and suspended in baghouses. Fabric filter allows dirty gases to pass through the fabric leaving the dirt in the form of a cake onto the outside surface of the fabric [2]. The layer of cake provides or acts as an additional filtering medium which further increases the performance of a collection of pollutants. Fabric filter is one of the popular options for particulate removal from gas streams by using an activated carbon as an adsorbent. Fabric filtration possesses several advantages such as smaller installation area, easier operation and lower operation costs [3].

In order to allow a uniform air flow passing through the filter media, pre-coating material needs to be applied to coat a layer of inert material onto each of the fabric as a barrier for protection from high-pressure drop [4]. In this study, the characteristics and physical properties of newly formulated filter aids material, a combination of PreKot™ and biochar were investigated. The materials work as a filter aid and simultaneously act as a flue gas cleaning agent which adsorbs VOCs as well as acid gases during flue gas treatment in a fabric filter.

2. Materials & Methods

2.1. Formulation of the new formulated filter aids material

Two main materials involved in the formulations are biochar (raw material) and PreKot™. Biochar was first grinded via a grinder from bamboo pieces into powder form. While, PreKot™ was purchased from a commercial company and was recently discovered by researchers in adsorption tests [4]. Formulations of these two main materials were based on the ratio of 10:90 and 20:80. Thus, samples that are going to be experimented for this study are biochar itself (as raw material), PreChar₁₀:₉₀ and PreChar₂₀:₈₀.

All samples were initiated by exposing the samples for about 5 hours. This is very important as it removes all undesired adsorbed gas and contaminants present in the materials. The formulated filter aids were kept and labelled in a covered bottle with a glass wool to avoid any additional moisture content. Thus, formulations are ready to be used to conduct experiments.

2.2. Characterization of the new formulated filter aids material

2.2.1. Moisture Content. Three formulated filter aids were weighed about 10 gram each and were left in the oven for 24 hours at 105°C. After 24 hours, the samples were weighed again to get the value of dried formulated filter aids. Moisture content in percentage calculated by following formula in equation (1).

\[
\text{Moisture content (\%) = } \frac{\text{Wi-Wa}}{\text{Wi-Wp}} \times 100
\]

Where:

- \( \text{Wi} \) = initial weight for petri dish with formulation (g)
- \( \text{Wa} \) = weight of petri dish with formulation after kept in oven (g)
- \( \text{Wp} \) = petri dish alone (g)

2.2.2. Brunauer-Emmett-Teller (BET). BET is a way to calculate the specific sample surface area (m²/g) including the distribution of pore size from gas adsorption by nitrogen gas. The volume of nitrogen gas adsorbed to the surface of the particles is measured at its boiling point (-196°C). At this temperature, nitrogen gas is below the critical temperature and so condenses on the surface of the particles. BET determines specific surface area using a single point on the isotherm. Micromeritics® 3 Flex Surface Characterization Analyzer model was used for this purpose.

For this study, adsorption on the adsorbent occurs in infinite layers. Basic concepts consist of constantly unchanged the heat of adsorption with the degree of coverage (\( \theta \)). Besides, the rate of
arrival of adsorption is equal to the rate of desorption. Total specific area will be determined in unit of m\(^2\)/g.

2.3. Adsorption performance test of the filter aids material in laboratory scale of fabric filtration system

Schematic diagram of the adsorption experimental set up displayed in Figure 1. It consists of concentrated toluene liquid, heat box, temperature sensor, adsorbent packed–glass (formulated filter aids), and portable VOC (ION, PhoCheck TIGER) with flow rate controller. The vaporized toluene flowed through the system towards the adsorbent vertically and the gas flow rate was controlled by the flow meter. The vacuum pump sucks the concentrated liquid toluene throughout the tube and gains the vaporized toluene. Vaporized toluene was then passing through the filter aids (adsorbent) before PVOC analyser. Then, concentration of vaporized toluene is the one will be measured by PVOC analyser.

![Schematic diagram of the adsorption experimental set up](image)

**Figure 1.** Experimental set up schematic diagram for toluene adsorption [5].

Experiments were run at three different flow rates 0.1 L/min, 0.3 L/min and 0.5 L/min and average reading was taken for further calculation adsorption capacity. For every test run, cleaning processes were done by flushing the set up. No samples involved during the flushing process and zero reading was achieved to ensure there is no toluene contaminant inside the system.

2.4. Adsorption capacity analysis

Adsorption capacities were calculated via integration of breakthrough curves. The value obtained between raw and filter aids formulations was compared for further research. In order to calculate breakthrough and equilibrium adsorption capacities per unit mass of adsorbent, equation below were be used:

\[
q = \frac{Q c_2}{M} \int_0^t \left(1 - \frac{c}{c_2}\right) dt
\]

(2)

Or simplified version is as following:

\[
q = \frac{Q c_{fS} - Q c_{fB}}{M}
\]

(3)
Where;
q = adsorption capacity in mg/g
\( t \) = time in min (break through point or saturation point)
M = the quantity of filter aids in g. M is 0.05 g which equivalent to 50 mg of filter aids used.
Q = gas flow rate (L/min)
C₀ and C₁ are initial and outlet concentration of toluene (mg/L)

3. Results & Discussion

3.1. Characterization of the new formulated filter aids material

Table 1 presented the moisture content of raw material (biochar) and formulated PreChar which has been demonstrated by percentage. PreChar_{20:80} presents slightly the same amount as biochar moisture adsorptivity. The difference in moisture content was influenced by the addition of the pre-coating agent. While, PreChar_{10:90} experienced the greatest amount of moisture content. Lower moisture content due to less carbon content in the formulation percentage influenced the moisture adsorptivity. In addition, determination of moisture content is necessary for long-term storage purposes in terms of adsorption. The filter aids materials are usually stored in a large container or silo and are continuously injected into a filtration system [6]. In case of high amount of moisture content of material stored, it tends to be denser and leads to caking problems inside the silo.

| Sample                | Moisture content (%) |
|-----------------------|----------------------|
| Biochar               | 3.417                |
| PreChar_{10:90}       | 4.427                |
| PreChar_{20:80}       | 3.306                |
| PreKot\textsuperscript{TM} | 0.730                |
| (N. Masdiana et al., 2017) |                     |
| Activated Carbon      | 23.390               |
| (N. Masdiana et al., 2017) |                     |

Surface area of a material is an important factor in heterogeneous chemical reactions and adsorption. The rate of adsorption of activated carbon material is directly proportional to the surface area. As adsorbate gas channels into the tube and passes through the adsorbent, it is expected that the maximum amount of contaminant from adsorbate gas will be adsorbed on the surface of adsorbent. Thus, larger surface area of material may boost the adsorption rate performance.

Figure 2 demonstrates the surface area of samples by using BET (Brunauer-Emmett-Teller) method. Filter aids formulations (both PreChar_{10:90} and PreChar_{20:80}) showed almost the same amount of surface area due to PreKot\textsuperscript{TM} addition. PreKot\textsuperscript{TM} extensively has large particle size in physical that will be discussed in further in subchapter (4.2.5) which relates to the particle size distribution of the material. Greater particle in size, lowering the surface area of the filter aids. Due to large particle size, both filter aids formulations experienced smaller surface area compared to biochar (raw material).
In addition, Masdiana et al. [7] and Hajar et al. [6] previously performed the activated carbon characteristic test which resulted in about 850 m$^2$/g which are higher compared to the samples in this study. Besides, the surface area of PreKot™ material is 2.52 m$^2$/g, has been discovered by Hajar et al. [4] on her formulation filter aids project. Specific surface area is an important feature in determining the chemical and physical interaction of the adsorbent with its surroundings. This is due to the fact that adsorption occurs on the particle surface.

3.2. Toluene adsorption performance on filter aids formulation and raw material

3.2.1. Biochar. Breakthrough time ($t_b$) is the time when the sorbent material begins to be saturated. While exhaustion time ($t_e$) is the moment when outlet concentration is almost similar with the initial concentration of vaporized toluene which indicates that adsorbent already fully saturated and blocked where adsorbate gas is not being adsorbed anymore. Figure 3 below demonstrated the breakthrough curves of biochar towards vaporized toluene.

Small arrow indicates the breakthrough time at 0.1 of $C_t/C_o$ as shown in figure 3. At 0.1L/min illustrated the longest period of breakthrough time, $t_b$ which is exceeding 5 minutes, while the shortest period belongs to 0.5L/min. This closely relates to the suction velocity of vacuum pumps where the higher flow rates will be capable to adsorb huge amounts of vaporized toluene. The shorter breakthrough time means that repetition of filter aids on fabric filters increases. Adsorption capacity differences between flow rates clearly affected approximately more than doubled. The adsorption capacity calculated showed that biochar are able to adsorb large amounts of vaporized toluene at 0.5 L/min. Fasten the suction flow rates, increasing the adsorbed gas capacity. 0.32493 mg/g defined as every 1 gram of biochar, 0.32493 mg of toluene succeed to be adsorbed.
3.2.2. PreChar\textsubscript{10:90}. PreChar\textsubscript{10:90} formulation resulted in a shorter breakthrough time where all three flow rates only took by less than 3 minutes. During 0.5 L/min, PreChar\textsubscript{10:90} has only approximately 1 minute before being starts to saturate by adsorbate attached to it. While, 0.1 L/min curve inclined extensively means it shows unstable condition during both adsorbate gas and filter aids meet together. It may be caused by the physical characteristic of PreChar\textsubscript{10:90} itself where it has larger particle size, high moisture content that eventually distorts the performance. Thus, PreChar\textsubscript{10:90} may be said to be the poor filter aids formulation to make contact with vaporized toluene based on its bad properties level among others.

Figure 3. Breakthrough curves of biochar adsorbed vaporized toluene liquid at three different flow rates.

Figure 4. Breakthrough curves of PreChar10:90 adsorbed vaporized toluene liquid at three different flow rates.
3.2.3. PreChar\textsubscript{20:80}. Breakthrough time of PreChar\textsubscript{20:80} by all different flow rates examined were exceeding 5 minutes which is great potential to obtain maximum adsorption rate. However, 0.1 L/min gained the longest period to reach the saturated point which is vice versa from biochar and PreChar\textsubscript{10:90} breakthrough time. Evidently, higher flow rates produce longer breakthrough time. Longer time to reach equilibrium points implies the capability of adsorbent to adsorb contaminated gas over a long period of time. By comparing both PreChar\textsubscript{10:90} and PreChar\textsubscript{20:80} adsorption capacity for each flow rate, PreChar\textsubscript{20:80} strongly described that it has high potential to adsorb vaporized toluene to the maximum level as it can. For instance, 0.5 L/min of PreChar\textsubscript{20:80} obtained almost 10 times bigger than PreChar\textsubscript{10:90} adsorbed vaporized toluene. More contaminants will make contact and attach on adsorbent surfaces. The increase in the dose may also cause aggregation of samples, consequently decreasing the availability of adsorption sites as well due to adsorption density [8].

![Figure 5. Breakthrough curves of PreChar20:80 adsorbed vaporized toluene liquid at three different flow rates.](image)

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