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Adsorption of Volatile Organic Compounds on Fluidized Activated Carbon Bed

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Background: Fixed bed adsorber as a controlling method for volatile organic compounds is widely used. However, these adsorbers are facing some issues such as high pressure drop, non-uniformed distribution of fluid, channeling and blockage. Fluidized bed adsorber as a novel method solves lots of these limitations.

Objectives: This research aimed at investigating factors affecting the adsorption of vapors of VOCs on fluidized bed adsorbers.

Materials and Methods: To assess adsorption, an annular fluidized bed reactor was designed and charged with activated carbon particles with size of 50 - 100 and 100 - 140 American society for testing and materials(ASTM) standard mesh, respectively. To calculate the minimum fluidization velocity, Ergun equation was used. The effect of inlet concentration (400 - 600 ppmv), fluidization velocity, particle size distribution and breakthrough time were investigated under a steady state.

Results: Tests indicated that by increasing flow rate from 0.3 (L/min), bubbles formed in the bed and the bed's pressure drop suddenly declined. The adsorption test indicated that, when Q = 3 (L/min), the removal efficiency of activated carbon (AC) (100 - 140 mesh ASTM), was nearly 100% up to 99 min and it reached zero after 260 min. For 50 - 100 Mesh AC, the removal efficiency was close to 100% up to 95 min and it reached zero after 270 Minutes. The results also indicated that increasing initial concentration and flow rate reduces breakthrough time. However, two flow rates, 2 and 3 (L/min) Comparison, did not reveal significant differences in the removal efficiency of the bed before breakthrough time.

Conclusions: Results indicated that annular fluidized bed reactor's adsorbers are useful techniques for VOCs adsorption. Comparison of two particle ranges indicates that in all concentrations and all flow rates of the experiments, smaller particle size adsorption are better. In superficial velocity above the minimum fluidization velocity, pressure drop of fluidized beds are less than the pressure drop of fixed beds. So fluidized bed systems are more applicable for smaller adsorber particles.

Keywords: Air Pollutants; Volatile Organic Compounds; Adsorption; Fluidized Bed; Activated Carbon

1. Background

Volatile organic compounds (VOCs) are the most abundant compounds in the atmosphere (1). These compounds could have macro perspective effects, such as climate change, increasing air pollution and effects on human's lives with several economic consequences. They can contribute to the formation of oxidants like ozone and peroxyacetyl nitrate (PAN) in the troposphere. Many of these compounds are known as carcinogens (1). Most of the chemical materials, which are used in industrial processes such as solvents, thinners, cleaners, lubricants and fuels, contain high levels of these compounds. VOCs are known as common pollutants in oil and petrochemical industries (2). Aromatic hydrocarbons (e.g. toluene, xylene, ethyl benzene), aliphatic hydrocarbons (e.g. n-heptanes and petroleum), ketones, esters, alcohols and glycols are among the most widely used VOCs (2). One survey on the residents of homes surrounding petrochemicals indicated that, living for more than five years increases the risk respiratory symptoms (3). Another study on gasoline station workers in Thailand indicated that, their risk of cancer increases due to exposure to VOCs (4). Also a survey on VOC exposure assessment in the shoemaking industry of China indicated that, despite the concentration decrease of benzene in this industry in recent years, the levels are still above the occupational exposure limit (OEL) (5). In addition, VOCs are known as one of the most common indoor environment pollutants which can be emitted from printers, building materials, equipment and cigarette smoking and can cause Sick Building Syndrome (SBS) (6, 7). Meanwhile Styrene is considered as one of the most widely used VOCs which is listed as a Hazardous Air Pollutant (HAP) under the Clean Air Act of the

Implication for health policy/practice/research/medical education:
The content and result of this paper is useful for researchers who are interested in air pollution control systems especially adsorption of volatile organic compound as pollutant using fluidized beds reactors.

National Emissions Standard Hazardous Air Pollutants (8). Styrene is primarily a synthetic chemical that is used extensively in the manufacture of plastics, rubber and resins. About 90,000 workers, including those who make boats, tubs, and showers, are potentially exposed to styrene (8). There are statistically significant differences in the styrene concentration across industries however the literature review shows that the hazard of dealing with styrene is more likely about 100 - 600 ppmv (8). There are several techniques for VOCs control, which can be divided into two categories: 1-Process equipment modification (for lower emissions), 2-use of control equipment which can be divided in to recovering techniques (e.g. adsorption) and destructive techniques (e.g. incineration, biodegradation and photo catalytic oxidation) (2, 9). Among these methods, adsorptions are widely used due to availability, ease of use and economical aspects (10). Selecting a suitable adsorbent is the primary step in the process of adsorption (2). The most important factors in determination of a suitable adsorbent are adsorption type, capacity, mass transfer rate, cost, abundance and recyclability (10). Activated carbon adsorptions are considered a common method of VOCs controlling with lower start-up cost compared to other similar controlling systems (2). Adsorption process of VOCs is usually carried out in fixed beds (11). However, performance of this system strongly depends on uniform distribution of air across the adsorbent and by clogging or channeling of flow, the efficiency is drastically reduced (9). As commonly known, adsorption process is exothermic and in the presence of high concentrations of compounds, the bed temperature increases and because of poor thermal conductivity of adsorbent particles, heat is usually limited to a small area of the bed and the temperature increases gradually. In some circumstances it can ultimately lead to fires and bed carbonization (9). High-pressure drop is another problem of packed bed adsorbers which is more noticeable in the high flow rate (12). Fluidized bed adsorber is considered as a new method of adsorption. In the fluidized bed adsorber, solid particles behave like boiling liquid. Fluidized bed is the best way for contacting different materials (12). Some advantages of a fluidized bed are complete mixing of particles, appropriate distribution of temperature, minimum temperature gradient across the bed (12), good performance achieved in a smaller volume (13), continuous process, purification of large volumes of gas, ability of filtering dust containing fluids, proper heat and mass transfer (11), low pressure drop, high surface area compared to a fixed bed (14), which ultimately leads to a higher performance.

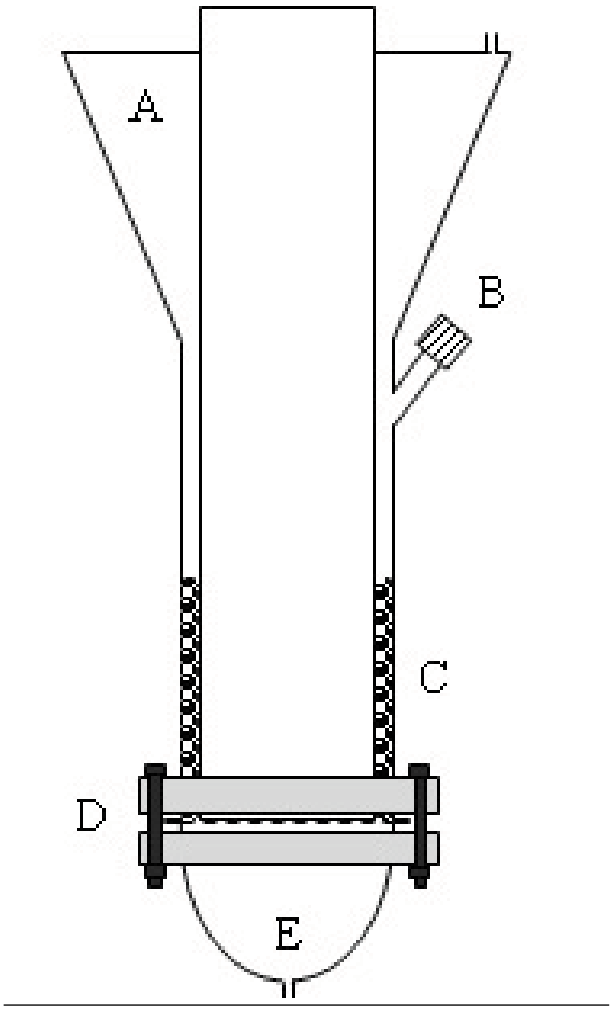
2. Objectives

In this study the adsorption of VOCs vapors in a fluidized bed has been investigated. The effects of factors such as flow rate, particle size, and concentration and adsorption capacity were investigated.

3. Materials and Methods

In this study, annular fluidized bed reactor systems which are shown in Figure 1, were designed to investigate the AC particles adsorption efficiency. In this experiment, inlet air was supplied by single lab pump. In order to remove probable air contamination, inlet air was passed through an AC and silica gel bed. The desired concentration was produced by the saturated vapor method. After stabilizing the concentration, vapors were injected below the annular fluidized bed reactor containing AC particles. The vapors after treatment were vented under the laboratory hood.

Figure 1. Annular Fluidized Bed Reactor Containing Activated Carbon Adsorbent Particles



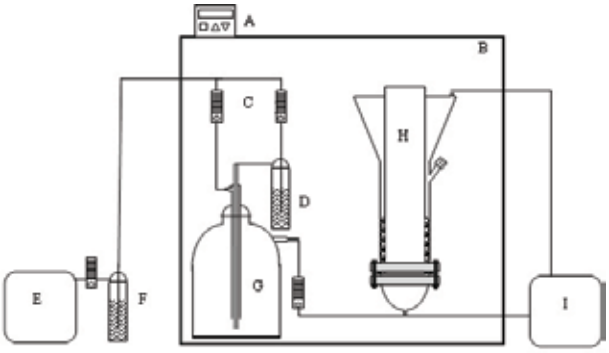
A) expanding area, B) screw cap, C) activated carbon particles, D) flange, gasket and gas distribiuter, E) gas inlet

3.1. Annular Fluidized Bed Reactor Design

Schematic design of the reactor, which was used in this study, is shown in Figure 2. For construction of the reac-

tor a 50 cm long Pyrex cylinder with 60 mm internal diameter was used and a 55 cm long cylinder with 55 mm outside diameter was installed. For uniform distribution of the gas flow in the lower part of the reactor, after reviewing several different distributors, a stainless steel gas distributor with a 6 cm diameter was designed and used. The distributor contained 12 holes with 2 mm diameters.

Figure 2. Schematic Diagram of Experiment Set Up



A) digital thermocouple, B) thermal box, C) rotameter, D) bubler of styrene, E) inlet air, F) granular activated carbon and silicagel, G) mixing chamber, H) annular fluidized bed reactor, I) gas analyser

To prevent the loss of AC particles from the lower part of the reactor, a standard screen mesh, 140 ASTM, was used. For this purpose, a circle with a 6 cm diameter of sieve screen was installed on a stainless steel plate and fixed. To empty AC from the bottom of the reactor, as shown in Figure 1, a flange with four bolts and nuts was used. The distance between the flanges was sealed with a silicone gasket. The distance between the gas inlet and the screen of particle was 10 cm. To prevent particles from leaving the fluidized bed reactor, the upper part of the reactor was built like a settling chamber. As shown in Figure 2, the upper part of the reactor was designed like a cone. In this mechanism, by increasing the outer wall diameter, the superficial gas velocity was decreased, so the probable escaped particles reached settling velocity and came back to the fluidized bed. In order to prevent the deposition of particles on the surface of the designed cone, experimentally, the cone's slope was set at 80 degrees. To add AC particles, a screw cap was designed in the body of the reactor (Figure 1).

3.2. Activated Carbon Adsorbent

In this study, the commercial activated carbon with an average particle size of 50 – 100, 150 -300 μm and 106 - 150 μm (ASTM standard mesh numbers 50 - 100 and 100 - 140, respectively) was used as a fluidized bed adsorber. To produce 1 kg of AC for each mesh size, 5 kg of cylindrical pellets, (AC 4 mm) were used. Cylindrical pellets AC was initially crushed by a crush roller to about 1 mm. Next, the particle was crushed by a ball mill and screened by ASTM standard sieve until the desired particle was achieved (8). To prevent more crushing of desired size particles in the crushing process, particles were separated from residues continuously by a standard sieve and vibration devices.

3.3. Calculation of the Minimum Fluidization Velocity

There are different methods to calculate the minimum Fluidization velocity (Umf) of particles and each one has its own precision (10, 13). In this study, in order to calculate the minimum fluidization velocity, the Ergun equation (Equation 1) was used (10).

$$\frac{1/75}{\varepsilon_{mf}^3 \varphi_s}\left(\frac{d_p\, u_{mf}\, \rho_g}{\mu}\right)^2 + \frac{150(1-\varepsilon_{mf})}{\varepsilon_{mf}^3 \varphi_s}\left(\frac{d_p\, u_{mf}\, \rho_g}{\mu}\right) = \frac{d_p^3\, \rho_g\, (\rho_s - \rho_g)\, g}{\mu^2}$$

Equation 1. Minimum Fluidization Velocity Calculate by Ergun Equation

In this Equation, the average particle diameter of activated carbon (dp) were considered 126.5 μm. Also density (ρS) and particles spherical ration (φS) were considered 480 Kg/m^3 and 0.8 respectively. For particles with average size of 126.5 μm, bed void space in minimum fluidization velocity (εmf) were considered 0.69 (8, 10). Reactor surface alignment is important in fluidization. Lack of reactor's surface alignment leads to bed inappropriate fluidity and fast leakage. The diameter of the cylindrical space of the reactor, in which the particles are located, should be equal in all parts; otherwise inconsistent fluidization may be created. In fact as the ring diameter decreases, the superficial gas velocity increases.

3.4. Concentration Generation Method and Analysis Technique

In order to generate stable concentrations of VOC, saturation vapors method was used. Monomer of styrene (Merck Co, Germany) was used, which is a colorless, odorless and oily VOCs with molar mass of 104.15 g, ρ = 909 Kg/m ^{3} , boiling point of 145 $^\circ$C and 4.5 mm Hg vapor pressure at room temperature 25 $^\circ$C. To generate constant concentrations in this study, all containers and connectors were placed inside a temperature-controlled box (Figure 2), based on Antoine's equation. The liquids vapor pressure depends on the temperature and the surface evaporation rate depends on the vapor pressure. Thus a heater thermostat system was used to control the temperature of the box. If the box temperature is reduced to 25 °C, the thermostat turns the heater on. In order to ensure proper operation of the system, chamber's temperature was continuously controlled

by an alcohol thermometer, which was placed inside of the chamber. In order to control the Midget Impinger's temperature, a sensitive electronic temperature (sensitivity factor 0.1) was placed on the Midget Impinger's wall which was controlled by an electronic thermostat (TMC 101, Plustek Inc., 1 digit accuracy). The container sensor acted quickly when temperature fell below 25 °C. Then a 40 w tape heater, which was wrapped around the Impinger, was quickly turned on. Digital thermostat system was equipped with a Proportional Integral Derivative (PID) mechanism. In this mechanism, the difference between the measured value and the desired value is calculated continuously, and the appropriate command is issued according to the increasing temperature gradient. The reactor inlet and outlet styrene concentration, were measured every 15 min by real time PhoCheck (model 5000, England) which uses Photo Ionization Detector (PID) mechanisms. In order to ensure the accuracy of the measured data, some samples were measured by GC (Philips PU-4410) equipped with a Flame ionization detector (FID) detector. Removal efficiency was calculated based on the reactor input and output concentration difference.

Removal Efficiency (%) = Input styrene concentration-output styrene concentration/Input styrene concentration

4. Results

In order to determine the minimum fluidization velocity, the inlet flow rate of the reactor was increased gradually and the static pressure of the reactor was measured continuously. Graphical relationship between the pressure drop of the AC bed (ΔP) across the flow rate (Q) is presented in Figure 3.

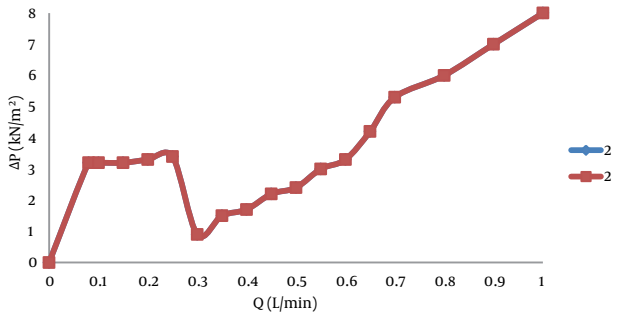


Figure 3. Graphical Relation Between Static Pressure Before the Activated Carbon Bed (ΔP) Across Flow Rate (Q) Adjusted by Flow Meter

Test results indicated that in a flow rate less than 0.25 L/min, the gas slowly passes through the void spaces of the particles. By increasing gas flow rate, superficial velocity increased and particles separated from each other or vibrated in their places. This condition is called the expanded bed. By increasing flow rate from 0.3 L/min, bubbles were formed in the bed and the bed's pressure drop suddenly declined due to the reduction of friction force. The Superficial velocity which cause AC particle to fluidize, is referred to as minimum fluidization velocity. Figure 4 Illustrates the removal efficiency of annular fluidized bed reactors containing ac in 400 ppmv styrene vapors concentrations and of 2 and 3 L/min flow rate. The removal efficiency of 6 g activated carbon with 100 - 140 standard mesh size, Q = 2 L/min, was nearly 100% in the first 115 min, however After 330 min, it reached zero, as shown in Figure 4. In the same way, the removal efficiency of 50 - 100 mesh size of AC, in the first 115 min of the test, was close to 100% and after 310 min, it became close to zero, relatively similar to 100 - 140 mesh size results. In the gas flow rate (Q = 3 L/min), the removal efficiency of activated carbon in the 100 - 140 mesh size, was nearly 100% in the first 99 min of the test and reached zero after 260 min. For 50 - 100 Mesh size in the initial, 95 minutes removal efficiency was close to 100% and after 270 minutes it reached zero.

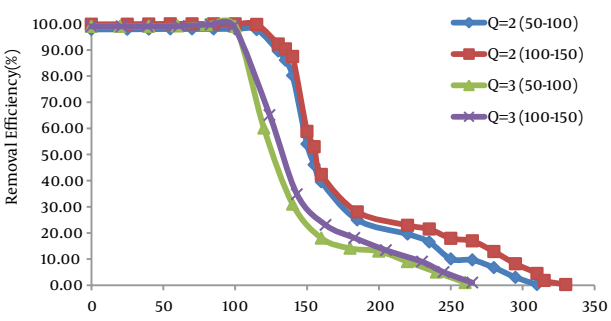


Figure 4. Effect Of Flow Rate On Fluidized Bed Removal Efficiency In Constant initial Concentration (C0 = 400 ppmv)

However comparison of the two different flow rates of Q = 2 and 3 L/min, did not reveal significant differences in the removal efficiency of the bed before breakthrough, and output concentrations were found to be similar at the beginning of both tests. Figure 5 Illustrates the reactor removal efficiency at Q = 3 L/min, and concentrations of 400 and 600 ppmv for the two particle size ranges of 50 - 100 and 100 - 140 μm. As shown in Figure 5, the reactor removal efficiency containing 6 g of 100 - 140 mesh size, which activated carbon in constant initial concentration (C0 = 400 ppmv), in the first 100 min of the test was 100% and after about 270 min, it reached zero. For the mesh size of 50 - 100, the removal efficiency was close to 100% in the first 98 min and after about 260 minutes, it reached zero.

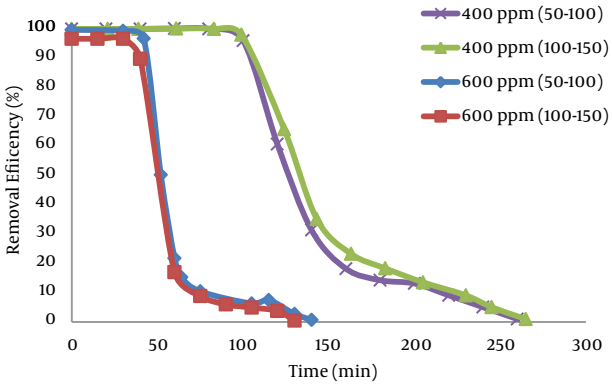


Figure 5. Effect of Initial Concentration on Removal Efficiency in Constant Flow Rate (Q = 3 L/min)

However, as shown in Figure 5, the reactor removal efficiency in constant initial concentration (C0 = 600 ppmv) for the 100 - 140 mesh size in the first 45 min of the test was nearly 100% and after about 140 min, it reached zero and for mesh size of 50 - 100, the removal efficiency of the first 40 min was nearly 100% and after about 140 minuts, it reached nearly zero. Furthermore, the results indicated that for all concentrations and flow rates, particles with size of 100 - 140 μm adsorption efficiency were greater than particles with size of 50 - 100 μm. The results indicated that in the process of fluidization, small part of AC is crushed due to attrition. Some of these particles are deposited in the chamber and are returned to the fluidized bed, but some particles are attached to the chamber walls due to static electricity and cover the body of the reactor as a thin layer or small part going out with the exhaust air. The average weight loss in 6 g AC during 5 hours fluidization tests was measured to be 0.12 ± 0.07 g.

5. Discussion

In the adsorption process, molecules physically adsorb to the activated carbon and separate from the gas stream. When all the pores of activated carbon are filled, it is not able to absorb more contaminants (2). Activated carbons are known as the most widely used adsorbers, because of their high surface area, large pore volume and low level of risk (10). AC adsorber systems are inexpensive, flexible and have lower start-up costs compared with other similar controlling systems (2). The relationship between static pressure of activated carbon bed (ΔP) across flow rate (Q) was used for the Umf prediction. In minimum fluidization velocity conditions, the compressive force of the upper particles disappeared and the bed pressure drop was approximately equal to the weight of the gas and suspended particles (12). In flow rates above the minimum fluidization velocity, ΔP increased almost linearly. Since decrease of particle size dramatically increased the pressure drop of fixed beds (12), it is not possible to use this size particles in the industrial scale of packed bed. However in superficial velocities above the Umf, pressure drop of fluidized beds are less than that of fixed beds. So fluidized bed systems are more applicable for smaller adsorber particles. Comparison of two different flow rates indicated that, at lower flow rates, longer times are needed for bed saturation and gas leakage, which is justifiable in terms of pollutant mass transfer. In studies conducted during 2009, the removal efficiency of toluene vapors in the annular fluidized bed reactor containing AC particles with 100 - 140 mesh size was close to 90% in the first 100 min of the test and after 180 min, it reached zero (15). Lack of reactor outlet concentration at the beginning of the tests, indicates that contact time of pollutant vapors and adsorber was sufficient for mass transfer and vapors had enough opportunity to adsorb to the bed. Comparison of two particle ranges indicates that for all concentrations and flow rates of the experiments, decreasing particle size led to an increase of adsorption efficiency. Studies conducted in the context of fixed bed activated carbon adsorption, also confirmed that decreasing the particle size, leads to increasing of the surface area and the adsorption efficiency (12, 16). Results showed that small parts of AC particles were crushed during the fluidization process due to attrition. Crushing of the AC samples depends on their resistance to abrasion. Studies show that, as the abrasion resistance of the particles becomes greater, fewer number of particles break and airborne (17, 18). Results indicated that by reducing the average size of particles, the adsorption capacity of the adsorbent increases. Hence, the use of smaller particles of AC in annular fluidized bed increases the efficiency of adsorption. One of the main advantages of fluidized bed adsorption systems is the ability to use small adsorbent particles. Comparison of fluidized and packed bed pressure drop indicated that at Superficial velocity above the minimum fluidization velocity, pressure drop of the fluidized bed are less than the pressure drop of the fixed bed. The effect of different operating parameters such as flow, initial concentration, adsorbent weight and mesh size of activated carbon particles in the fluidized bed reactor indicated that, increase in initial concentration and flow rate reduces breakthrough time. However increase in adsorbent weight can increase breakthrough time. Finally From the comparison of fixed and fluidized bed adsorbers it can be concluded that in smaller adsorbent particles, a fluidized bed system is more applicable.

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Authors' Contribution

Amirabbas Mofidi (50%), Hassan Asilian (30%), Ahmad Jonidi Jafari (20%).

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