

PREPARATION OF ACTIVATED CARBON FROM WALNUT SHELL AND ITS UTILIZATION FOR MANUFACTURING ORGANIC-VAPOUR RESPIRATOR CARTRIDGE

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ABSTRACT

Walnut shell, as an agricultural by-product, was processed and optimized to develop high surface area activated carbons by chemical activation, using KOH to obtain high efficient adsorptive properties for VOCs.

Surface and textural characterizations of activated carbon were respectively investigated by BET technique at a low temperature (77°K) of nitrogen and Scanning Electron Microscopy (SEM).

Activated carbon prepared from walnut shell with an activation ratio of 1.7 and at a temperature of 700°C gave the highest BET surface area (737 m²/g) and adsorptive values of 43.40±2.62, 57.60±4.51, 64.80±3.98, 64.70±2.16, and 64.95±2.25 mg BTXs/g activated carbon for benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene respectively.

The granular form of prepared activated carbon having maximum adsorption value was employed in organic vapor respirator cartridges for respiratory protection. Break-through time of 85 minutes was measured based on the EN 14387:2004 conditions for respiratory protection.

This study showed that activated carbon adsorbents made from walnut shell can be produced at optimized conditions and successfully employed for the removal of VOCs from air in respirator cartridges.

KEYWORDS: Organic vapour, Respirator, Cartridge, Walnut shell, Activated carbon

1. INTRODUCTION

Volatile organic compounds (VOCs) are a class of chemical pollutants in the environment, causing severe health problem. Some of the VOCs like Benzene, Toluene, Xylenes (BTXs) are even known or suspected as carcinogens and need some effective control strategies to be developed [1, 2].

Adsorption of contaminants on sorbents is one of the most important methods for controlling VOCs exposure. Activated carbon (AC) is the most versatile and frequently used sorbent in the form of fixed bed for environmental control because of its large internal surface area and pore volume as well as its ability to absorb organic vapors at low cost. These characteristics have made it as one of the most practical adsorbents [3, 4]. Also, activated carbon is used with air-purifying respirators to remove toxic gases and vapours from inspired air as a personal protective device. These cartridges and canisters contain activated carbon granules in a packed bed which adsorb organic vapours from air when they pass through the sorbents [5]. The typical organic vapor half-mask respirator cartridge is a plastic or metal case which contains 25-40 g of activated carbon, which, sometimes is impregnated with metallic salt to enhance its acid gas adsorption characteristics.

Adsorption of toxic substances in a respirator depends on the nature of activated carbon, including the porosity, chemical structure of the carbon surface, the nature of the impregnate, and the method of impregnation [6].

Modification and impregnation techniques of AC can be used for increasing the surface adsorption, removal capacity, and the improvement of the selectivity to organic compounds [7].

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Basically, there are two different processes for the preparation of activated carbons: the so-called physical and chemical activations [8, 9].

Chemical activation only involves a single step in the heating process (carbonization process) to activate the carbon. This process needs chemical activating agents such as $ZnCl_2$, KOH , H_3PO_4 or H_2SO_4 to enhance the carbon yield and produce micropores on the surface of the carbon. These agents will increase the surface area and reduce the ash content of the final carbonized products. As a result of the pyrolysis process, much richer carbon content material as well as much more ordered structure is produced. After the heat treatment, once the chemical agent is eliminated, the porosity will be developed. Physical activation involve oxidizing the raw material at high temperatures in the presence of an oxidizing agent, usually, water steam. As this is an endothermic reaction, a constant $800^\circ C$ temperature must be maintained. This process needs two steps of heating to be performed and does not involve any chemical treatment. However, the surface properties and pore characteristics must be enhanced by the carbonization process [10-13].

Major advantages of the chemical activation compared to physical activation are lower treatment temperatures, as well as shorter treatment times. In addition, activated carbon obtained by the chemical activation exhibits a larger surface area and a better meso porosity than the physical activation [8, 9].

Usually, all carbons used in the respiratory protective devices originates from coconut shell or petroleum-based materials, because they exhibit a highly developed microporous surface required for maximum adsorption [14].

Iran is the third largest producer of walnuts in the world, producing 10% of the of walnuts on the market [15], so, walnut shell can be used as an alternative source for production of activated carbon.

The scope of the present study was to prepare activated carbon from walnut shell through chemical activation at optimized weight ratios and temperatures for adsorption of VOCs and test the effectiveness of the prepared activated carbon in granular form in the respirator cartridges for respiratory protection in relevant occupational processes.

2. MATERIALS AND METHODS

2.1. Activated carbon preparation

Walnut shell was used as the carbonaceous source material to prepare of activated carbon. Potassium hydroxide was used as the activating agent, because it is considered as the most effective compound in the production of activated carbons [9, 12, 16].

Walnut shells with an initial particle size of 0.21–0.35 mm were crushed, milled, and screen-sieved. Then, they were mixed with potassium hydroxide in different weight ratios (activation agent/walnut shell) and were heated up to different temperatures (see Table 1). This was followed by allowing the walnut shells to soak the potassium hydroxide, heating for 2 hours, and drying in an oven at $150^\circ C$. Each impregnated sample was carbonized in a quartz tubular reactor, vented to the atmosphere, and heated in an electrical furnace. The samples were then heated up to the activation temperature under N_2 flow at a specified heating rate and held for a specified period of time at the activation temperature.

After activation, the samples were cooled down under N_2 flow and washed out twice with a 0.5 N hydrochloric acid and, finally, rinsed sequentially with cold distilled water to remove the residual chemical substances. The washed samples were then dried at $110^\circ C$ in an oven [17]. Activation conditions (weight ratios and activation temperatures) were chosen based on available literature [7, 18].

2.2. Characterization of activated carbon sample

Samples were subsequently degassed at $150^\circ C$ for 8 hours. Barrett-Joyner-Halenda (BJH) pore size distribution and BET specific surface area of the adsorbents obtained were determined by nitrogen adsorption isotherm at $77^\circ K$, using a Micromeritics ASAP 2010 instrument.

The surface of the samples were observed using a scanning electron microscope (SEM, Cambridge S-360 operated at 16 kV and 2.5 Å).

2.3. Volatile Organic Compounds (VOCs) adsorption

1000 ppm of BTXs, as representative VOCs was used, to determine the adsorption value of the powdered form of the prepared adsorbents, as this is a typical maximum use concentration (MUC) of organic vapour in respirator cartridges [19].

TABLE 1 - BET surface area, pore properties and adsorption value of samples at different activation conditions

Sample	R (weight ratio)	Activation Temp. $^\circ C$	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	Adsorption value (mg/g) [M \pm SD]				
						Benzene	Toluene	<i>o</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene
K1-450	1	450	478	0.26	21.9	28.81 \pm 3.81	35.11 \pm 2.57	39.81 \pm 2.37	39.89 \pm 3.58	40.11 \pm 2.04
K1-700	1	700	502	0.316	24.9	30.11 \pm 2.07	39.15 \pm 3.56	40.25 \pm 2.15	42.11 \pm 2.18	41.72 \pm 2.05
K17-450	1.7	450	498	0.330	26.5	35.90 \pm 4.27	43.40 \pm 3.06	48.80 \pm 2.41	37.90 \pm 3.42	46.80 \pm 2.74
K17-700	1.7	700	737	0.404	21.95	43.40 \pm 2.62	57.60 \pm 4.51	64.80 \pm 3.98	64.70 \pm 2.16	64.95 \pm 2.25
K2-450	2	450	650	0.317	19.5	36.80 \pm 2.05	44.60 \pm 2.94	49.40 \pm 2.37	48.70 \pm 3.74	47.90 \pm 2.89
K2-700	2	700	723	0.347	18.8	40.11 \pm 2.91	51.60 \pm 4.35	59.80 \pm 3.93	58.70 \pm 3.56	60.95 \pm 4.60

Figure 1 shows the experimental set up for the adsorption experiments. Model air samples were generated by injection of 84 microlitres of a BTX mixture (using a 100µl syringe) into a 5-liter Tedlar-bag previously filled with hydrocarbon-free air under ambient pressure. The injection valve was immediately closed and the bag heated in an oven at 80°C for 1 hour. Adsorption studies were conducted using the following method [20].

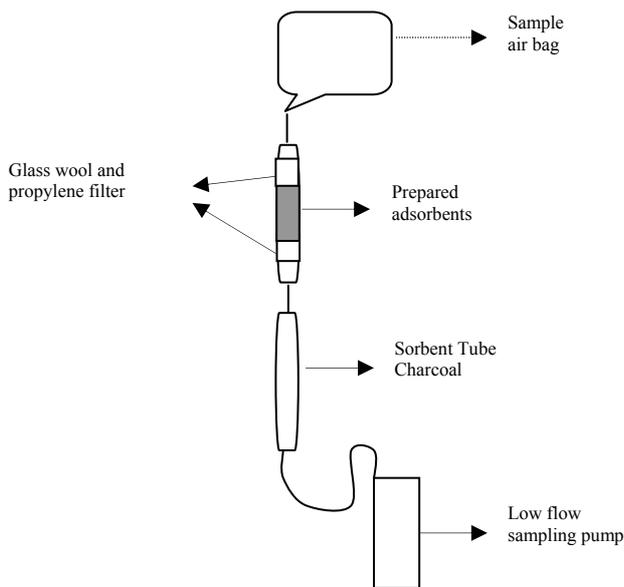


FIGURE 1 - Schematic experimental set up for adsorption experiments

Prior to the experiment, the adsorbent samples were degassed at 200°C for 8 hours to remove moisture or gases trapped in the samples. Then they were homogeneously packed into a 9-cm length glass column (internal diameter 10mm). Silane-treated glass wool and propylene filters

were used at both ends of the column to hold the adsorbents in place. The final mass of adsorbent in each column was approximately 80 mg. The inlet end of the adsorbent-column was connected to the sample bag. The other end was connected to the charcoal sorbent tube (Anasorb CSC, SKC) to trap any adsorbate not retained by the adsorbents in the column.

An SKC low flow pump connected at the end of the tube provided an adjustable flow rate through the system.

To measure the amounts of BTXs trapped by the charcoal, they were extracted using carbon disulfide (CS₂) and analyzed using a Shimadzu gas chromatography system. The BTXs adsorbed on the adsorbents were estimated by subtracting of the BTXs retained on the charcoal from the initial quantities injected into the sample bag. Each adsorption experiment was conducted in triplicate for each sample.

2.4. Granular activated carbon

Because of the difficulties in handling, the pressure drop, and the powdered form of the adsorbent obtained, it was not appropriate for use in respirator cartridges. In order to convert it into a granular form, the adsorbent was mixed with a suitable carbonaceous binder (just enough to allow kneading and homogeneous mixing) and manually extruded. The granular adsorbent was then carbonized in an oven at 800°C overnight and, finally, activated with CO₂ for 8 hours.

Forty grams of prepared granular adsorbent with an average granule size of 0.11 cm and a packing density of 0.43 g/cm³ were used to prepare the material suitable for the respirator cartridge with a bed depth and a diameter of 3 and 7.4 cm, respectively.

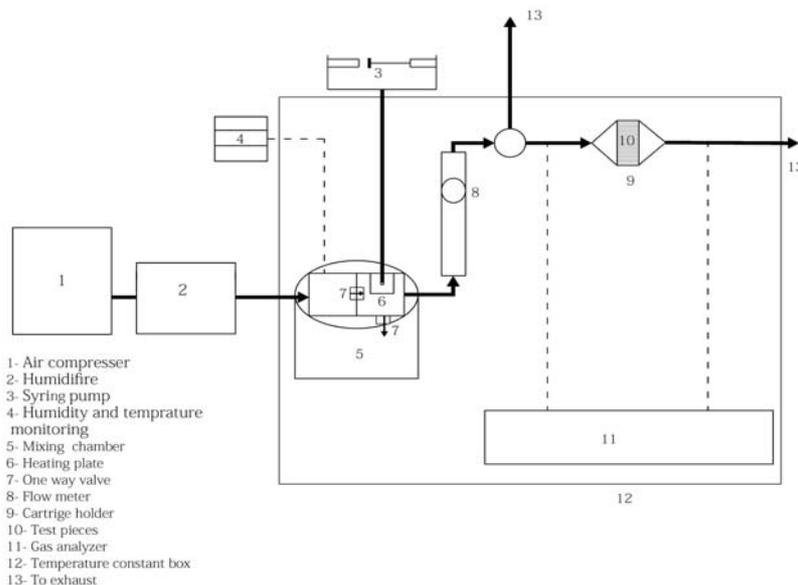


FIGURE 2 - A schematic diagram of the apparatus for measuring the breakthrough times of respirator cartridge

2.5. Cartridge breakthrough time testing

For measuring the breakthrough time of the respirator cartridges, they were exposed to cyclohexane (as a representative organic vapour) according to the EN 14387:2004 standard [21], with the aid of the apparatus illustrated in Figure 2.

The main part of this apparatus was the mixing chamber, made of PTFE, consisting of three parts. The first part was equipped with temperature and relative humidity sensors (TC4Y-14R, Autonics, Korea); the second part accommodated a heating plate (item 6) to vaporize the solvent as it entered from the syringe pump (model HX-901A, item 3). After humidification, the air (item 2) passed through the first part to the second, mixed with vaporized solvent and, then, entered the third part (item 5, the main part of mixing chamber).

These parts were clamped together with an o-ring to provide a leak-proof fit, and two one-way valves (items 7) between the parts prevented back pressure inside the chamber.

Inlet air was provided by an air compressor, filtered for organics and particulates, and was passed through a humidifier to control and maintain a constant humidity in the mixing chamber. The air temperature and relative humidity were adjusted at $25 \pm 2.5^\circ\text{C}$ and $70 \pm 2.5\%$, respectively.

The mixing chamber output was directed into the cartridge holder where the adsorbent test material was placed. At the start of the run, the mixing chamber output was bypassed to a vent (item 13). After adjusting both the temperature and humidity at a steady state concentration,

based on the desired values, (which normally took 30 min.), the bypass valve was shut, the air stream was allowed into the main line, and the test was started.

The concentration of cyclohexane vapour was regulated in the range of 1000 ± 10 ppm by controlling the injection rate of the syringe pump.

The vapour concentration of cyclohexane was measured both upstream and downstream of the cartridge, using a gas analyzer equipped with a Photo Ionization Detector (Ion Sciences Co., UK).

The interval between the start of the test flow and the time when the vapour concentration downstream of the respirator cartridge reached a value of 10 ± 2 ppm was recorded as the breakthrough time.

3. RESULTS AND DISCUSSION

3.1. Characterization of Activated Carbon

The adsorption/desorption isotherms for nitrogen of the prepared samples are shown in Figure 3. As it can be seen, the greater the surface area of the sample, the higher the quantity of the nitrogen absorbed.

Table 1 presents the surface areas and pore structures, as well as the adsorption values of the carbon samples activated by KOH. Table 1 shows that various degrees of improvement of the surface area and pore volume may be achieved to different extent after activation of the carbon. Generally, the specific surface areas of activated carbon are increased by chemical and physical activations.

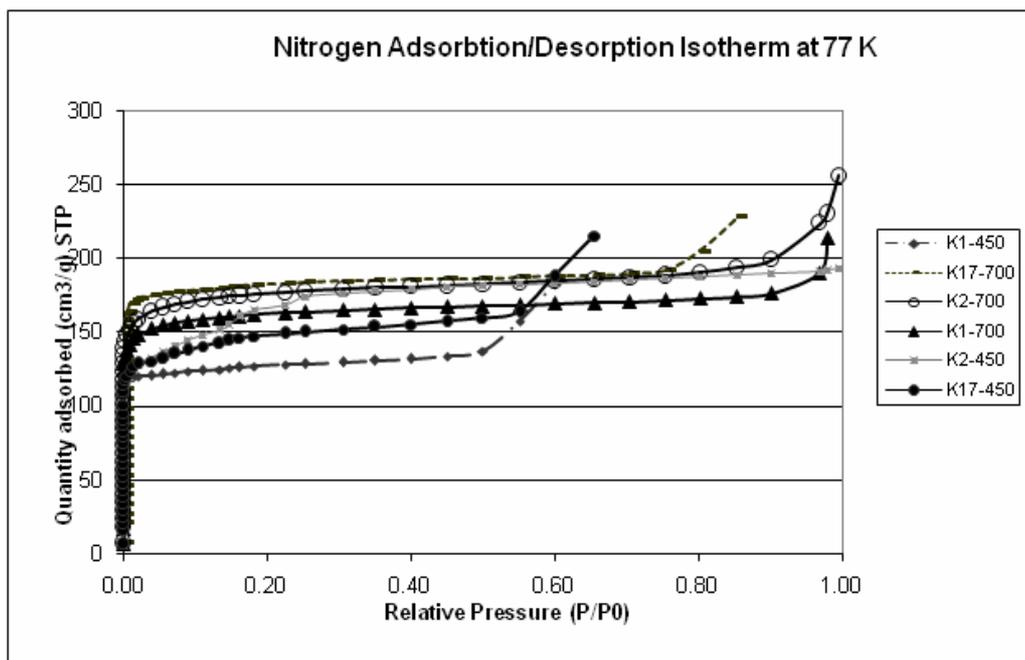


FIGURE 3 - Nitrogen adsorption/desorption isotherms of prepared activated carbons

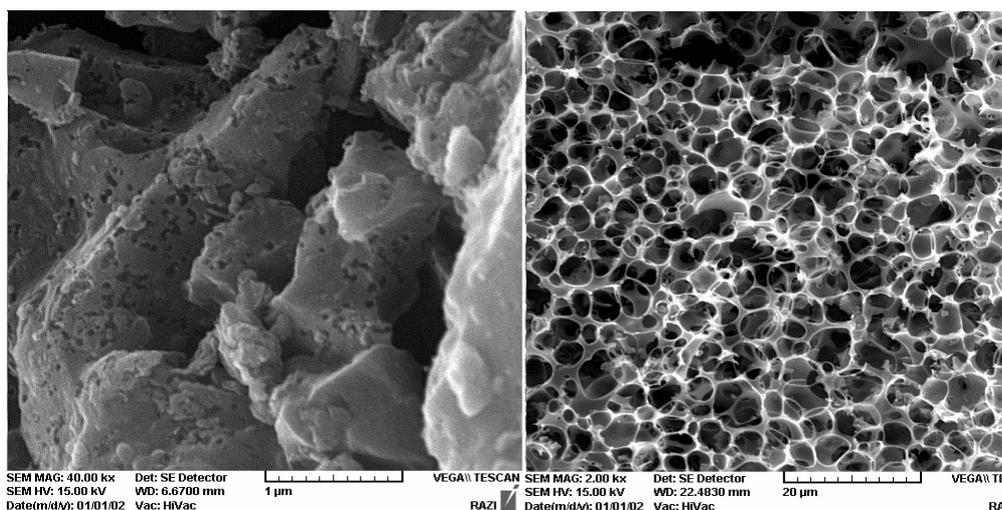


FIGURE 4 - SEM micrographs of optimum sample of prepared activated carbon (K17-700)

Since the molecular size of all sorbates of this study were smaller than 1 nm (0.58 to 0.68) [23], microporosity, is an important parameter affecting their adsorption. Therefore, higher adsorption of K17-700 in comparison with other prepared samples could be attributed to its higher micropore volume.

The most suitable conditions to prepare activated carbons were found to be a temperature of 700°C and impregnation with KOH at a weight ratio of 1.7, namely, as K17-700, which gives the highest nitrogen adsorption, the highest surface area of 737 m²/g, and a total pore volume of 0.404 cm³/g.

Elemental analysis by energy dispersive X-ray analysis (EDS) showed 93% carbon in the optimum sample of prepared activated carbon (K17-700). This high value of the carbon element shows the good quality of carbonization process.

Figure 4 shows the SEM micrograph of the porous structure of optimum sample of prepared activated carbon (K17-700).

The absorption values of the various adsorbents prepared are illustrated in Table 1. It is seen that, adsorption value increases remarkably with increasing the ratio of the activation agent to walnut shell. This finding conform that reported by Hu and Vansant [22] who also found the weight ratio to be the most important parameter in producing activated carbon

Table 1 also shows that higher activation temperatures are more effective in development of larger surface area with a higher pore volume and adsorption value. Therefore, it can be inferred that an increase in the activation ratio and the activation temperature leads to an increase in the surface area and porosity of the activated carbon obtained.

Further analysis of the data showed that the sample activated with KOH, with a weight ratio of 1.7 and at a temperature of 700 °C gave the highest adsorption value by adsorbing 43.40±2.62, 57.60±4.51, 64.80±3.98, 64.70±2.16, and 64.95±2.25 mg BTXs/g activated carbon for benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene, respectively (Table 1). The high adsorptive value of this sample could be associated with its high surface area and pore volume. Therefore, this sample with a surface area of 737 m²/g and a pore volume of 0.404 cm³/g was selected for preparing the material for the test respirator cartridge in granular form.

Table 2 shows the cyclohexane breakthrough time of the cartridges prepared in different bed depths and adsorbent masses. As it can be seen, breakthrough time increased in a higher bed depth and adsorption mass. The average breakthrough time of the cartridge with a bed depth of 3cm (corresponding to an adsorbent mass of 40 gram) was 85 minutes (Figure 5). Therefore, this cartridge meet the minimum breakthrough time of 70 min for respirator cartridges as defined by the EN 14387:2004 Standard.

TABLE 2 - Cyclohexane breakthrough time of cartridges prepared from walnut shell based activated carbon in different bed depth and adsorbent mass

Breakthrough time (min) [M±SD]	Adsorbent weight (g)	Bed depth (cm)
15±2.12	14	1
50±3.53	27	2
85±4.24	40	3

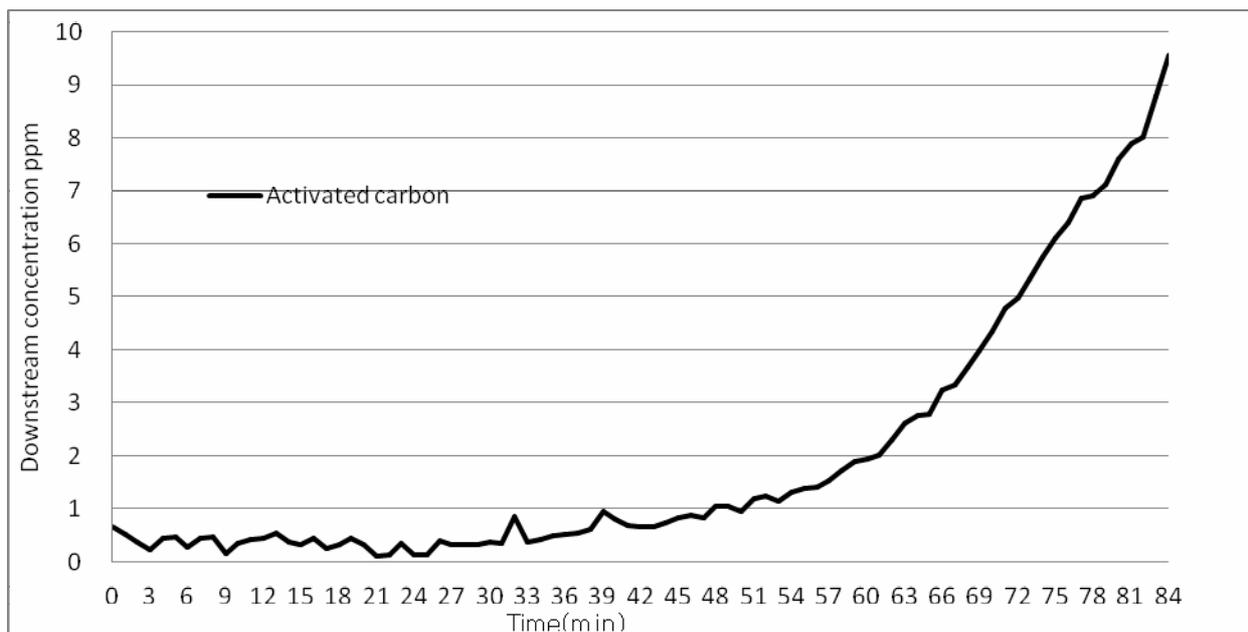


FIGURE 5 - Breakthrough time of cartridge prepared from walnut shell based activated carbon (K17-700)

4. CONCLUSION

Activated carbon was prepared through chemical activation of walnut shell with potassium hydroxide, tested for VOCs adsorption, and successfully employed in respirator cartridges in a granular form. The cyclohexane breakthrough time of the cartridge prepared was higher than the minimum breakthrough time allowed in respirator cartridges as defined by the EN 14387:2004 standard. Therefore, this adsorbent is recommended as an alternative adsorbent for the respirator cartridges in the future.

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REFERENCES

- Heidari, H.R., Shahtaheri, S.J., Golbabaie, F., Alimohamadi, M. and Rahimi-Froushani, A. (2008) Optimization of head-space solid phase microextraction procedure for trace analysis of toluene. *Int. J. Occup. Saf. Ergon. (JOSE)* 14, 365-375.
- Heidari, H.R., Shahtaheri, S.J., Golbabaie, F., Alimohamadi, M. and Rahimi-Froushani, A. (2009) Trace analysis of xylene in occupational exposures monitoring. *Iran. J. Public Health.* 38 (1),89-99.
- Prakash, J., Nirmalakhandan, N., Speece, R.E. (1994) Prediction of Activated Carbon Adsorption Isotherms for Organic Vapors. *Environmental Science & Technology* 28, 1403-1409.
- Mohan, N., Kannan, G.K., Upendra, S., Subha, R. and Kumar, N.S. (2009) Breakthrough of toluene vapours in granular activated carbon filled packed bed reactor. *Journal of Hazardous Materials* 168, 777-781.
- Moyer, E.S., Smith, S.J. and Wood, G.O. (2001) Carbon Tetrachloride Replacement Compounds for Organic Vapor Air-Purifying Respirator Cartridge and Activated Carbon Testing: A Review. *AIHAJ - American Industrial Hygiene Association* 62, 494 - 507
- Roop Chand Bansal, M.G., (2005) Activated Carbon Adsorption.
- Alvim-Ferraz, M.C.M., Todo-Bom Gaspar CM (2003) Impregnated active carbons to control atmospheric emissions: I. Influence of the impregnated species on the porous structure. *Journal of Colloid and Interface Science* 259, 133-138
- Lozano-Castelló, D., Lillo-Ródenas, M.A., Cazorla-Amorós, D., Linares-Solano, A. (2001). Preparation of activated carbons from Spanish anthracite: I. Activation by KOH. *Carbon* 39, 741-749.
- Sricharoenchaikul, V., Pechyen, C., Aht-ong, D. and Atong, D. (2007) Preparation and Characterization of Activated Carbon from the Pyrolysis of Physic Nut (*Jatropha curcas* L.) Waste, *Energy & Fuels* 22, 31-37.
- Hu, Z. and Vansant, E.F. (1995) Chemical activation of elutriite producing carbon-aluminosilicate composite adsorbent. *Carbon* 33, 1293-1300.
- Ahmadpour, A. and Do, D.D. (1996) The preparation of active carbons from coal by chemical and physical activation. *Carbon* 34, 471-479.



- [12] Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A (2003): Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. *Carbon* 41, 267-275.
- [13] Kim, K.J., Kang, C.S., You, Y.J., Chung, M.C., Woo, M.W., Jeong, W.J., Park, N.C., Ahn, H.G. (2006) Adsorption-desorption characteristics of VOCs over impregnated activated carbons. *Catalysis Today* 111, 223-228.
- [14] Nelson, G.O. and Correia, A.N. (1976) Respirator cartridge efficiency studies: VIII. summary and conclusions. *American Industrial Hygiene Association Journal* 37, 514 - 525
- [15] Food and Agriculture Organization of the United Nations (FAO). 2005 [Available from: www.faostat.org].
- [16] Evans, M.J.B., Halliop, E. and MacDonald, J.A.F (1999) The production of chemically-activated carbon. *Carbon* 37, 269-274.
- [17] Namvar-Asl M, Soltanieh M, Rashidi, A. (2008) Modeling and preparation of activated carbon for methane storage II. Neural network modeling and experimental studies of the activated carbon preparation. *Energy Conversion and Management* 49, 2478-2482.
- [18] Martínez, M.L.M., Agnese, M. and Guzman, C. (2003) Making and Some Properties of Activated Carbon Produced from Agricultural Industrial Residues from Argentina. *Journal of the Argentine Chemical Society* 91, 103-108.
- [19] NIOSH (2009) Respiratory Protective Devices, 42 CFR Part 84.
- [20] Jahangiri, M., Shahtaheri, S.J., Adl, J., Rashidi, A., Kakooei, H., Rahimi Forushani, A., Ganjali, M.R. and Ghorbanali, A. (2011) The adsorption of benzene, toluene and xylenes (BTX) on the carbon nanostructures: the study of different parameters. *Fresenius Environmental Bulletin*, 20 (4a), 1036-1045.
- [21] EN14387 (2004) Respiratory protective devices. Gas filter(s) and combined filter(s). Requirements, testing, marking.
- [22] Hu, Z. and Vansant, E.F. (1995) Synthesis and characterization of a controlled-micropore-size carbonaceous adsorbent produced from walnut shell. *Microporous Materials* 3, 603-612
- [23] Aguado, S., Polo A.C., Bernal, M.P., Coronas, J.I. and Santamar, A.I. (2004) Removal of pollutants from indoor air using zeolite membranes. *Journal of Membrane Science* 240, 159-166.

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