Adsorption of Benzene, Toluene, Ethylbenzene and o-Xylene by Carbon-Based Adsorbents

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Article info

Abstract

This study explored the possibility of applying different carbon-based adsorbents for removal of benzene, toluene, ethylbenzene and o-xylene (BTEX) from indoor air in static and dynamic modes. To determine BTEX removal effectiveness, the approach based on solid-phase microextraction (SPME) in combination with gas chromatography – mass spectrometry (GC-MS) was used. In static mode, removal effectiveness of BTEX from indoor air using different carbon-based adsorbents (shungite, walnut shell, saxaul, apricot pits, activated charcoal, Tenax, carbon black) varied from 80% to 100%. Optimal preparation conditions for shungite-based adsorbent are no activation and addition of NaOH at 1:0.8 ratio. Shungite-based adsorbent was not able to remove BTEX from polluted indoor air at the flow rate 300 mL/min corresponding to the linear flow rate 25 cm/s, a minimum value for most commercial air purification systems. At the flow rate 75 mL/min (6.25 cm/s), a saturation time of shungite-based adsorbent made up 368 min for benzene and 437 min for toluene. At this flow rate, BTEX adsorption capacities of the shungite-based adsorbent were 0.3, 2.1, 0.2 and 0.3 μg/g, respectively. Compared to shungite, activated charcoal allowed the complete removal of BTEX at both flow rates in the whole studied time frame. Thus, shungite-based adsorbents are not recommended for BTEX removal from air because of much greater efficiencies of classic activated charcoal adsorbents. Applied methodology based on SPME-GC-MS allowed simple, fast and inexpensive collection of data and can be recommended as the analytical tool for developing new adsorbents and systems for air purification.

1. Introduction

Rapid population growth, urban sprawl, increased energy usage and transportation cause serious air pollution in many cities around the world [1]. One of the most hazardous compounds among volatile organic compounds (VOCs) are benzene, toluene, ethylbenzene and xylenes (BTEX) [2–4]. Main sources of BTEX are transportation, power plants, industrial enterprises, and construction works [5–7]. Humans are exposed by BTEX through a respiratory system and skin contact [8].

People spend more than 80% of their time indoors [9]. Concentrations of VOCs in indoor air are higher than outdoors, because indoor air pollutants originate both from ambient air and other emission sources including construction materials, paints, furniture, electronics, household cleaning products [10–12] and human-exhaled breathing air. Therefore, indoor air pollution is associated with higher human health risks often leading to sick building syndrome (SBS) [13].

Indoor air quality (IAQ) can be improved by upgrading ventilation system and/or air purification by sorption, thermal, catalytic and photocatalytic oxidation, negative air ions/nonthermal plasma, and biofiltration. After purification, indoor air quality may become better than that of outdoor air. Sorption is the most economical and simple method for improving IAQ. Compared to other methods, sorption does not lead to formation of harmful by-products during purification. Sorbents based on activated carbon (AC), zeolites and silica gel provide an effective BTEX removal from air [14, 15]. AC filters (ACFs) showed an effective adsorption of BTEX from inert gaseous stream and have a longer

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lifetime than zeolites and silica gel under identical operation conditions [15]. ACFs are reusable and may be regenerated – 90–95% of trapped toluene can be desorbed from sorbent by purging with ambient air at 7–18 °C and relative humidity of 50–80% [16]. Activated carbon can be regenerated at 120–180 °C to return 50% of initial capacity, further regeneration is complicated by lack of desorption from smallest pores of carbon [17].

Commercial air cleaning systems are applied worldwide for improving indoor air quality (Table 1). Most of them are based on ACF's. Tion O2 (Tion Inc, Russia) is equipped with adsorption-catalytic filter. Among all commercial systems, detailed test report is available only for Tion O2 system providing 84% toluene removal from its initial concentration of 264 mg/m^3 being 2–4 orders of magnitude higher than typically observed values for indoor and outdoor air. Phresh Filters (Phresh Filters, Australia) are cylinders made of stainless steel and loaded with 46 mm in diameter RC-48 activated carbon pellets. Compared to competitors, their design allows working at lower linear flow rates at volumetric flow rates from 240 to 4260 m^3/h. In Winix PlasmaWave 5300 (Winix Inc, IL, USA), after ACF, ionizer is installed as a third stage (ACF dimensions 43 cm × 33.3 cm × 6.3 cm).

There are limited data on a removal of low concentrations of BTEX from "real" air [18, 19]. Most studies were focused on high concentration ranges of BTEX and were carried out in controlled laboratory conditions [20, 21].

According to the review articles [18–22], none of the available technologies was able to effectively remove all VOCs from indoor air. Ao et al. [23] established less than 10% toluene removal at 2 ppm concentration using commercially available air cleaner unit (not specified). Wan-Kuen Jo [22] increased breakthrough time of benzene and toluene removal by fibrous activated carbon from 7 to 13 h (two times) using UV light-emitting diodes. TiO$_2$ is popular agent for sorbent modification [18, 19] – the sorbent acts like a local concentrator for further photo degradation under UV treatment. TiO$_2$ coupled with ACF showed 3–36% more effective BTEX removal than single TiO$_2$ filter [23] and fibrous activated carbon (FAC)/ TiO$_2$ composite showed 65–70% more effective BTEX removal than single FAC filter [22]. Sidheswaran et al. [24] achieved ~97 h of VOCs adsorption (toluene, benzene, o-xylene, 1-butanol, limonene, undecane and formaldehyde in range of 20–30 ppb) by activated carbon fiber (Calgon corp., 80 × 0.4 mm, 1000–2000 m^2/g) having total VOC's capacity of 91 mg/g.

Linear flow rate affects the cleanup effectiveness [25]. At higher linear flow rates, pollutants in an air steam have a shorter contact time with a sorbent, which decreases the probability of contaminants' adsorption. More effective adsorbents should allow purification at higher linear flow rates. On the other hand, lower flow rates allow using smaller adsorbent particles having higher sorption capacity and providing higher purification effectiveness [25]. If an air purification unit is combined with a system of forced ventilation, it should be capable of working at flow rates 20–60 m^3/h per person in the room to satisfy hygienic standards. For Tion O2 unit having filter size 40 × 10 cm, linear flow rate via the ACF at 30 m^3/h will be 20.8 cm/s. At enhanced filter thickness 5 cm, air will pass the filter for just 0.25 s.

There are a lot of sources presented as AC precursors, such as date pits [26], cotton stalks [27], peach stones [28], almond shells [29], olive stones [30], coconut shell [31] and shungite [32]. They show close to commercial activated carbon's surface areas: 652-1669, 600-800, 608-1404, 527-733, 1151 and 245 m^2/g for date pits, cotton stalks, peach stones, almond shells, coconut shell and shungite, respectively.

Shungite is abundant and inexpensive local resource may be used as a cheaper alternative to ACFs. There is the currently explored "Koksu deposit" in Kazakhstan with proven reserves of shungite equal to 49 M tons. The carbon content in shungite rocks varies from 6 to 27%. Carbon content can be increased to 38–44% after concentration by foam flotation [33] with acid and up to 92% by thermally treatment (carbonization) in inert atmosphere (Ar) at 550–650 °C. The main advantage of CB shungite is low cost (aprox. 130 $ per 1 ton) in comparison with activated charcoal (4,500 $ per ton) [32]. Carbon-based (CB) shungite sorbents were successfully applied for adsorption of phosphine, ammonia, hydrogen sulfide and cyclohexane from generated gas stream. Adsorption capacity of composite CBS for cyclohexane and phosphine were 12 (0.35 L/min, 0.1%) and 11 mg/g (1 L/min, 300 mg/m^3), respectively [32].

In addition, shungite with different carbon content (from 4% to 70%) was tested for o-xylene adsorption from generated air [34]. Adsorption capacity of sorbents increased from 0.1 to 450 mg/g with increasing of carbon content in shungite from 4 to 70%. Increasing the temperature of adsorption from 20 °C to 100 °C decreased the adsorption capacity of carbon-based shungite adsorbent (70%) from 450 to 45 mg/g. At 200 °C, xylene adsorption did not occur [34]. Adsorbents based on shungite are reusable and may be regenerated at 200–250 °C [34].

Table 1
Description of commercially available air cleaning systems

Air purification system	Filter shape and dimensions, cm	Purification effectiveness, %	Cleaning duration, months	Volumetric flow rate, m³/h	Linear flow rate*, cm/s	Experimental testing parameters
Aeropac SN	Parallelepiped	>90	4	10–170	7–135	-
Tion O2	Parallelepiped, 45×16×1	80–99	12	35–120	14–47	$C_{(toluene)}$ = 264 mg/m³ T = 24 °C, relative humidity 25%, flow rate 117 m³/h
Phresh	Cylinder, 10.04×20.08- 35.14×125.5	-	24	240–4260	20–30	-
IQAir Health Pro	Parallelepiped, 32.63×32.63×12.55	<70*	16	190–475	35–90	-
GermGuardian AC4825	Parallelepiped, 40.9×12.2×1.5	-	-	170	95	-
Winix Plasma-Wave 5300	Parallelepiped, 43×33.3×6.3	-	12	100	20	-

Note: *Data is calculated from provided parameters in manual (passport or system description)

The introduction of impregnating solutions increases cleaning effectiveness of adsorbents due catalytic properties of modified sorbents. Kabulov A.T. et al. [32] showed the increase of efficiency of phosphine, ammonia, hydrogen sulfide adsorption (80%) by using carbon-nickel (7%), carbon-cooper (10%) composite porous sorbents from shungite. However, there no data about using modified (with metal additives) shungite based sorbent for BTEX removal from indoor air.

The objective of this work was to compare benzene, toluene, ethylbenzene, o-xylene removal effectiveness (%) from indoor air using different carbon-based adsorbents (shungite, walnut shell, saxaul, apricot pits, activated charcoal, Tenax, carbon black).

2. Experimental

2.1. Standards and solvents

Benzene (99.8%) and toluene (99.8%) were obtained from EKOS-1 LLP (Moscow, Russia). Ethylbenzene (99.0%), and o-xylene (99.0%) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Methanol (HPLC grade) was obtained from AppliChem (Darmstadt, Germany). Helium (>99.995%) was purchased from "Orenburg-Tehgas" (Orenburg, Russia).

2.2. Methodology of analysis

Solid-phase microextraction (SPME), very popular and widely applied method all around the world due to its simplicity and reliability [35, 36], was used for controlling concentrations of BTEX before and after air purification in combination with gas chromatography – mass spectrometry (GC-MS).

In this work, two types of SPME fibers were used – 65 μm Polydimethylsiloxane/divinylbenzene (PDMS/DVB) for experiments on static adsorption and 85 μm Carboxen/polydimethylsiloxane (CAR/PDMS) for dynamic adsorption. The latter is known to provide the greatest BTEX extraction effectiveness [37, 38]. Extraction conditions are provided in the descriptions of each experiment.

All extractions were conducted using a Combi PAL (CTC Analytics AG, Switzerland) autosampler installed on the 6890N/5973N (Agilent, Santa Clara, USA) GC-MS equipped with split/splitless inlet. Thermal desorption of analytes from SPME fiber in GC injector was done in splitless mode at 250 °C using 0.75 mm i.d. liner (Supelco, USA) during 5 min. Separation of BTEX was done on a 60 m × 0.25 mm DB-WAXetr (Agilent, USA) column with a film thickness 0.50 μm at the constant flow of He (1 mL/min). Temperatures of MS ion source, quadrupole and interface were 230, 150 and 250 °C, respectively. Oven temperature was programmed from initial 40 °C (held for 1 min) to 160 °C (held for 2 min) at the heating rate of 10 °C/min. GC column retention times for BTEX were 8.6, 10.3, 11.8 and 12.8 min, respectively. Detection was carried out in selected ion monitoring (SIM) mode at m/z 78, 91, 106 and 106 for selective detection and quantification of the four BTEX constituents, respectively. Total GC run time was 15 min.

2.3. Methods of preparation of adsorbents for the analysis

In the present work, sorbents based on mineral and vegetable raw materials were tested. Shungite rock was obtained from the "Bolshevik" deposit located in the Eastern Kazakhstan. As carbon-vegetable raw materials, saxaul, walnut and apricot were used. Widely used adsorbents Tenax (Supelco, Bellefonte, PA), carbon black (Supelco, Bellefonte, PA) and activated charcoal were studied for comparison.

Enrichment of shungit rock was performed by the method of froth flotation using flotation machine FM-1 (TRUD Facilitiy, JSC, Novosibirsk, Russia). This method allows separation of the mineral and the carbon component of shungite. Pine oil (Mirrolla, Ltd, Saint-Petersburg, Russia) and kerosene were used as flotation reagents. After concentration by foam flotation, carbon content increased to 38–44% (wt.).

After drying at 140–150 °C, shungite powder was mixed with dry NaOH at different mass ratios (1:0.8 and 1:1) followed by addition of distilled water and drying during 24 h at 70 °C. Then binder (molasses sugar, Burunday Sugar Factory, Ltd, Almaty, Kazakhstan) was added to dry concentrate at the concentration of 10% for forming the pellets. Pellets (10 mm length and 0.4 mm diameter) were obtained by extruding the concentrate from 10 mL syringe. Then, pellets were thermally treated (carbonized) in inert atmosphere of argon at 700 °C during 1 h for carbonization of molasses sugar.

The obtained adsorbent was activated with water vapor at a temperature of 800–850 °C in the activation heater during 60 min, steam flow rate was 1 L/h to 200 g of adsorbent. The increase in specific surface area occurs due to the burn out of unstructured carbon [33].

Saxaul was pre-crushed in a rotary knife mill RM 120 (Vibrotehnik Ltd., Saint-Petersburg, Russia). Carbonization and activation by acute water vapor were carried out according to the same method as for the sorbents based on mineral raw materials.

2.4. Static adsorption

Prior to sampling, 1.00 g of adsorbents were pre-conditioned in 20 mL crimp-top vials (HTA, Italy) at 200 °C during 2 h and then sealed with aluminum caps with PTFE-Silicone septa (Zhejiang Aijiren Technology Co., ltd, China) for preventing the adsorption of analytes present in laboratory air. Masses and the diameters of used adsorbents are shown in Table 2.

1.00 µL of standard solution containing 0.2 ng/µL of benzene and toluene and 0.02 ng/µL of ethylbenzene and o-xylene in methanol were injected into enclosed vials with lab air to obtain concentrations of analytes standard additions in gas phase 100 µg/m^3 for benzene and toluene and 10 µg/m^3 for ethylbenzene and o-xylene. Then samples were kept for 60 min at room temperature (25 ± 2 °C) without shaking. The extraction was performed by 65 µm DVB/PDMS fiber for 1 min at 23 °C. Low extraction time was chosen to avoid extraction of analytes from sorbents and extract only analytes present in air above sorbent. All samples were analysed in two replicates (separate vial for each measurement) using SPME-GC-MS.The scheme of the single sample processing in static mode is presented in Fig. 1.
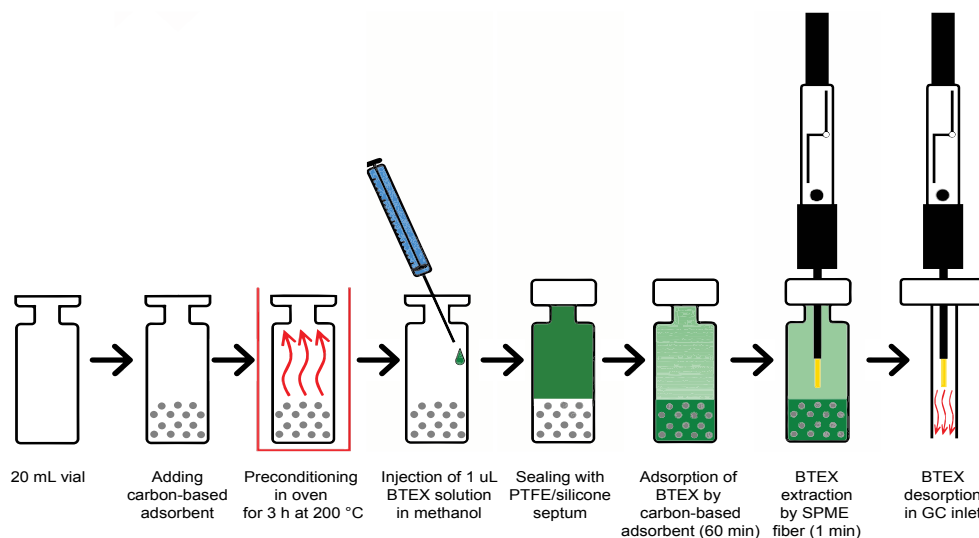

Fig. 1. Methodology for testing adsorbents in static mode.

Table 2
Characteristics of the used adsorbents

#	Sorbent type	Particle size, mm	Mass, g
1	Walnut shell (WSh)	0.315	1.000
2	Apricotpits (AP)	0.315	1.000
3	Apricotpits (AP)	Not ground	1.053
4	Shungite (Sh)	0.63–4.00	1.000
5	Activated charcoal (AC)	0.4–4.0	1.000
6	Saxaul (S)	Not ground	1.000
7	Tenax (T)	~0.04	0.130
8	Carbon black (CB)	~0.04	0.150

2.5. Dynamic adsorption

System for dynamic adsorption was assembled as shown in Fig. 2. The system consisted of Jun-Air OF302 (JUN-AIR, Inc., USA) compressor, 5 mm internal diameter and 25 cm length glass tube, 20-mL vial sealed with magnetic cap and PTFE-Silicone septa (Agilent, Santa Clara, USA), and 250-mL bubble flow meter. The vial was modified with input and output ports by a glass-blowing workshop at the Institute of Combustion Problems (Almaty, Kazakhstan).

Dynamic sorption of BTEX from the laboratory air was performed at 20–25 °C. The mass of adsorbent in glass tube was ~1.3 g and the thickness of a sorbent layer was constant (12 cm) by fixing it with glass wool from both sides of glass tube. Addition

of BTEX was not required due to sufficient concentration in laboratory air (18–27, 40–51, 1–2, 2–8 μg/m^3 for BTEX, respectively). Air before and after cleanup with adsorbent were extracted by SPME fiber in the sampling vial using the Combi PAL (CTC Analytics AG, Switzerland) auto sampler. Air sampling was conducted using 85 μm CAR/PDMS fiber for 3 min.

Lab air was pumped into the system at 300 and 75 mL/min flow rate. Flow rate 300 mL/min provides linear flow rate 25 cm/s, which is close to those in commercial air purification systems working at flow rates >20 m^3/h required according to sanitary standards [39]. Flow rate 75 mL/min was tested because air purification from BTEX by shungite-based adsorbent was not observed at 300 mL/min.

3. Results and discussions

3.1. Adsorption of BTEX on carbon-based sorbents in static mode

In the static mode, walnut shells and activated charcoal have the greatest BTEX adsorption effectiveness (Fig. 3). Both sorbents completely adsorbed ethylbenzene, o-xylene and benzene. Relative residual concentration of toluene was 0.4% and 0.6% for walnut shell ash and AC, respectively. Commercial sorbents Tenax and carbon black showed good affinity to o-xylene and ethylbenzene (100%), and absorbed 77–79% of benzene and 99% of toluene.

Unground apricot pits (sample #2) (size ≤3 mm) adsorbed a greater mass of BTEX – 91%, 99%, 100%, 100%, respectively. Ground faction of apricot pits (sample #1) adsorbed 81%, 93%, 98%, 97% of BTEX, respectively. This was probably due to stronger matrix resistance to BTEX diffusion to the lower layers of the ground fraction [25]. The product of carbonization of saxaul (sample #9) showed
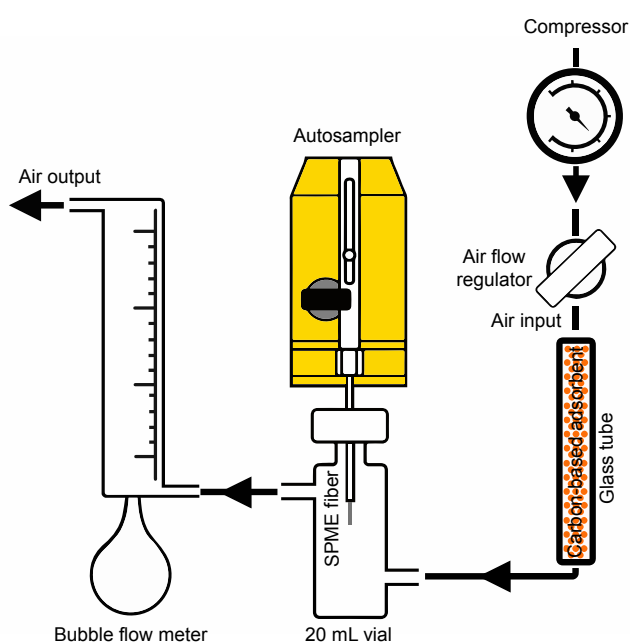

Fig. 2. Experimental setup for testing adsorbents in a dynamic mode.

similar adsorption effectiveness of analytes (88%, 95%, 83%, 82%) with a great value of a standard deviation, that may indicate the difference in surface morphology in comparison with other studied sorbents – adsorbent did not equilibrate in one hour, probably due to a slower inner diffusion comparing to other studied adsorbents. Two rise husk samples (#13 and #14) carbonized at 500 and 700 °C adsorbed 92, 99, 100, 100 and 93, 99, 100, 100% of BTEX. Probably, temperature above 500 °C does not provide more complete burn-out of this raw material.

Shungite (sample #10) provided complete removal of o-xylene and ethylbenzene like most studied sorbents – apricot pits, activated charcoal, Tenax, carbon black and walnut shell, and also adsorbed 96% of toluene. However, concentration of benzene decreased by only 13% which is less effective in experiment. This can be explained by a poor porosity of shungite (was not measured in this work) that is crucial for adsorption of small molecules. Thus, it was found that the best adsorption of BTEX was observed for activated carbon and walnut shell ash.

Different modifications of shungite (sample #8, #9, #11 and #12) showed different results. Shungite (samples #11 and #12) not activated by vapor provided 98, 100, 100, 100 and 96, 99, 100, 100%

BTEX removal for 1:0.8 and 1:1 NaOH ratios, respectively. Vapor-activated shungite (samples #8 and #9) provided 98, 100, 100, 100 and 97, 99, 100, 100% BTEX removal for 1:0.8 and 1:1 NaOH ratio, respectively.
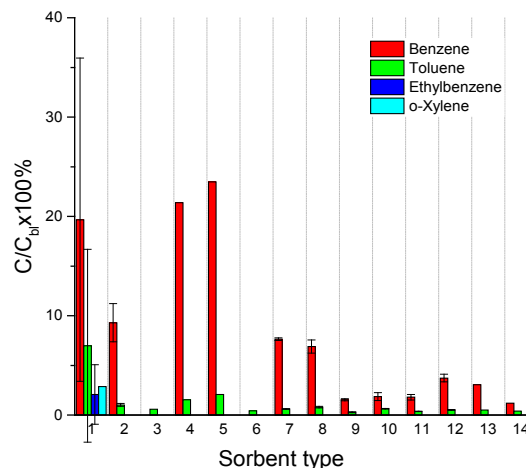

Fig. 3. Adsorption of benzene, toluene, ethylbenzene and o-xylene by carbon-based adsorbents in static mode: 1 – apricot pits (0.315 mm); 2 – apricot pits; 3 – activated charcoal; 4 – Tenax; 5 – carbon black; 6 – walnut shells; 7 – shungite (NaOH 1:0.8, act); 8 – shungite (NaOH 1:1, act); 9 – saxaul; 10 – shungite; 11 – shungite (NaOH 1:0.8); 12 – shungite (NaOH 1:1); 13 – rise husk carbonized at 500 °C; 14 – rise husk carbonized at 700 °C
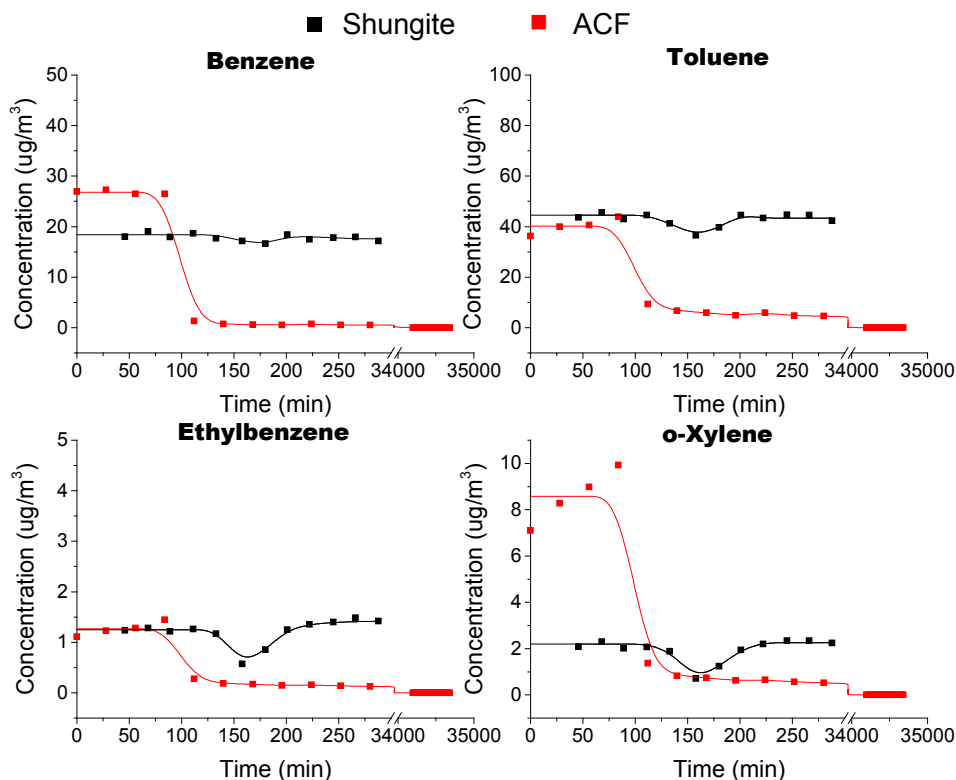

Fig. 4. Dynamic adsorption of BTEX from lab air by shungite-based and activated charcoal adsorbents at flow rate 300 mL/min.
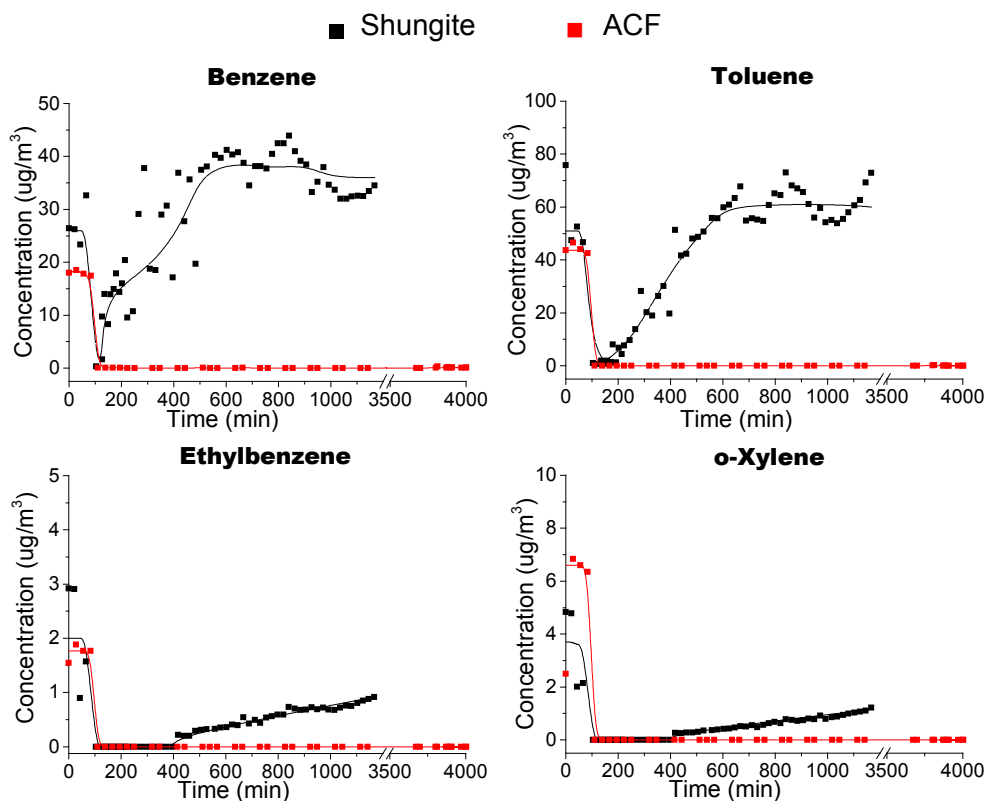
Fig. 5. Dynamic adsorption of BTEX from lab air by shungite-based and activated charcoal sorbents at flow rate 75 mL/min.

All tested adsorbents showed 80–100% BTEX removal, activated charcoal and walnut shell ash show absolute BTEX removal. Optimum preparation conditions (no activation, NaOH 1:0.8) for shungite-based adsorbent were established.

Shungite-based adsorbent, which provided 96–100% BTEX removal, was selected for next experiments due to its potential to become a cheaper alternative to the activated charcoal on the market of adsorbents.

3.2. Adsorption of BTEX in dynamic mode

Shungite-based adsorbent showed no BTEX adsorption at the flow rate of 300 mL/min (Fig. 4).The activated charcoal sorbent provided complete removal of BTEX from air during one month, probably caused by its greater BTEX trapping capability.

As known, a linear flow rate significantly affects the process of adsorption of analytes to the surface of carbon-based adsorbents. After air flow was decreased from 300 mL/min (25 cm/s) to 75 mL/min (6.25 cm/s), a saturation time of shungite-based adsorbent made up 368 min for benzene and 437 min for toluene (Fig. 5). Adsorptive capacity of shungite-based adsorbent calculated by integration of the obtained plots (Fig. 5) using the trapezoidal rule was 0.3 and 2.1 µg/g for benzene and toluene, respectively. Extrapolation of ethylbenzene and

o-xylene curves resulted in adsorptive capacities 0.2 and 0.3 µg/g for ethylbenzene and o-xylene, respectively. These values are much lower than 1.8 and 8.9 mg/g for benzene and toluene, respectively, as reported by Wan-Kuen Jo et al. [40]. Activated charcoal adsorbed all BTEX during one week of the experiment. The significant adsorptive capacity difference between AC and shungite-based adsorbent can be explained by the difference in surface area being 1000 m^2/g and 245 m^2/g, respectively.

Thus, currently available shungite-based adsorbents do not provide sufficient effectiveness compared to classic activated charcoal sorbents. However, the technology for their production is relatively new, and it has a potential for improvement. In addition, for improving the air purification effectiveness, these adsorbents may be coated by known photochemically active reagents (e.g., TiO$_2$) or transition metals additives [23, 41].

4. Conclusions

Thus, removal of BTEX from indoor air by different carbon-based adsorbent was studied in static and dynamic modes using solid-phase microextraction in combination with GC-MS. In a static mode, removal efficiencies of BTEX from indoor air using different carbon-based adsorbents (shungite, walnut shell, saxaul, apricot pits,

activated charcoal, Tenax, carbon black) varied from 80% to 100%. Optimal preparation conditions (no activation, NaOH 1:0.8) for shungite-based adsorbent were established. Adsorbent obtained at these conditions provided 96–100% BTEX removal and was selected for experiments on adsorption of BTEX in dynamic mode.

In dynamic mode at 300 mL/min (25 cm/s), shungite-based adsorbent did not provide any BTEX removal from polluted air. At 75 mL/min (6.25 cm/s), a saturation time of shungite-based adsorbent made up 368 min for benzene and 437 min for toluene. At these conditions, adsorptive capacity of the shungite-based adsorbent was 0.3, 2.1, 0.2 and 0.3 μg/g for BTEX, respectively. Compared to shungite, activated charcoal allowed the complete removal of BTEX at both flow rates in the whole studied time frame. This can be explained by the difference in surface area being 1000 m^2/g and 245 m^2/g, respectively.

Thus, shungite-based adsorbents are not recommended for BTEX removal from air because of much greater efficiencies of classic activated charcoal adsorbents. To achieve similar effectiveness, a technology should be developed for increasing surface area and porosity of shungite materials. In addition, shungite-based adsorbent can be modified by photochemically active reagents (e.g., TiO$_2$) or transition metals.

Applied methodology based on SPME-GC-MS allowed simple, fast and inexpensive collection of excessive information about the process of air purification from trace concentrations of BTEX. Experiments in dynamic mode were completely automated and allowed obtaining high-quality plots. Thus, the used approach can be recommended as the analytical tool for developing new adsorbents and systems for air purification. It can be further extended by increasing the number of monitored analytes including polycyclic aromatic hydrocarbons, phenols, halogenated hydrocarbons and other known air pollutants.

Acknowledgements

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