



Benzene extraction in environmental samples based on the mixture of nanoactivated carbon and ionic liquid coated on fused silica fiber before determination by headspace solid-phase microextraction-gas chromatography

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ABSTRACT

In this study, the mixture of nano activated carbon (NAC) and ionic liquid (3-triphenylphosphonio-propane-1-sulfonate; $C_{21}H_{21}O_3PS$) was coated on fused silica fiber of SPME holder (NAC-IL-FSF/SPME). Then NAC/IL was used for determining of benzene in soil and vegetables samples (1.0 g, $n=50$) surrounding a chemical industry zone. After benzene adsorption on NAC-IL based on head space solid phase microextraction (HS-SPME), the concentration of benzene was simply determined by introducing probe to injector of gas chromatography with flame-ionization detection (GC-FID). All effected parameters such as the sorbent mass, the amount of sample, the temperature, and the interaction time were optimized in glass chromatography vials by static procedures. The benzene vapor was absorbed from soil and vegetables samples with NAC-IL-FSF/SPME holder for 10 min at 80°C (10 mg of NAC and 0.1 g of ionic liquid in 0.5 mL of acetone coated on FSF). Then the benzene was desorbed and determined by GC-FID spectrometry. The extraction efficiency and absorption capacity of adsorbent were obtained 98.5% and 127.2 mg g⁻¹, respectively. The high surface area of NAC and favorite interaction of aromatic chain in IL (π - π), caused to efficiently remove of benzene vapor by HS-SPME procedure as compared to other nanostructures.

1. Introduction

Recently different sources of volatile organic compounds (VOC's) such as benzene released in atmospheric air. VOC's consist of dangerous compounds which were produced due to the leaking gasoline vapor from the car engine or

other chemical activity [1-4]. The main material of refrigerants, plastics, adhesives, paints, and petroleum products is composed of VOCs [5]. VOC's such as benzene effect on human health and caused cancer in human body [6-8]. For many years, the analysis of trace volatile organic compounds (VOCs) in exhaled breath could potentially provide rapid screening procedures to diagnose and monitor the diseases of the lungs. The previous research showed that the earlier detection VOCs with GC-

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MS caused to decrease the different types of cancer in human body. The most diagnostic tools cannot detect the cancer disease in primary stages. Various types of biomarkers including peptides, DNA, RNA, and cells are used in the diagnosis of cancer in human body [9]. The high concentration of BTEX (benzene, toluene, Ethylbenzene, Xylenes) can be absorbed by skin, lungs and gastrointestinal system from air, waters and foods. The VOCs can be accumulated in liver, renal, and CNS and caused to dysfunction in human organs. Benzene vapor cause to lymphoma, anemia, the acute leukemia in humans and classified as high risk factor material which was reported by international agency for research on cancer (IARC) [10,11]. The different cancers may be generated by exposure to benzene in the indoor air. Among the BTEX compounds, benzene is the most dangerous material and cause to bone damage, dysfunction of CNS, damage of liver and respiratory tract. Based on US occupational safety and health administration (OSHA) and centers for disease control and prevention, national institute for occupational safety and health(NIOSH), the average of 1.0 ppm benzene in air was selected as the permissible exposure limit (PEL) [12]. Many techniques such as extraction, adsorption, degradation, the catalytic oxidation, the adsorptive concentration-catalytic oxidation, the photocatalytic oxidation, and the plasma catalytic oxidation were used for removal and determination of VOCs in water samples [13]. The important sources of benzene include, the petroleum company, benzene tanks, petrochemical factories and gas pipes [14]. Moreover, the low value of BTEX compounds in the water, soil and vegetables is very hazardous and must be controlled [15]. Nanoparticles (NPs) have been highly used for removal of environmental pollutants such as VOCs from air and waters. Due to the unique properties of NPs, the adsorption processe was obtained with high efficiency and recovery [16]. The cupric oxide nanoparticles (CuONPs) have been used for adsorptive removal of benzene and toluene from aqueous environments [17]. Due to previous studies, the different methods such as, adsorption [18,19], the photo-catalytic oxidation and thermal

oxidation [20] were used for removal of VOC's or BTEX in environment matrixes. Teimoori et al (2020) showed that the benzene can be extracted and determined in waters and wastewater samples based on functionalized carbon nanotubes (R-CNTs) using GC-FID. They observed that under optimal conditions, the adsorption efficiency of CNTs@PhSA and CNTs for benzene was obtained 97.7% and 20.6 % in water samples, respectively [15]. Recently, the activated carbon based on micro pores and heterogeneous surface functional groups was used for benzene extraction in environmental samples such as water and wastewater samples [21, 22]. Also, the activated carbon was most commonly used as absorbent for VOC's removal from air and waters. By previous researches, the adsorption capacity of activated carbon was reported and depended on its surface area, pore volume, porosity and chemical functional groups. In addition, the other nano-carbon structures such as MWCNTs, graphene (NG) and carbon quantum dots (CQDs) were used for BTEX removal from environment matrixes [23, 24].

In this study, the novel adsorbent based on NAC-IL coated on FSF/SPME holder was used for benzene extraction/separation/determination in soil and vegetables samples by HS-SPME procedure coupled to GC-FID. Validation methodology was confirmed by spiking of samples.

2. Experimental

2.1. Apparatus

Gas chromatography based on air /gas loop injection with flame ionization detector was used for benzene analysis in air (Agilent GC, 7890A, GC-FID, Netherland). The sampling valves introduced a sample into the carrier gas stream and valves were also used to inject sample gases/ liquids in gas streams. The split/split less injector, FID detector, and a column of PDS (50 m × 0.2 mm; poly dimethyl siloxane) were selected for benzene determination by Agilent GC. The ultra-pure hydrogen gas (H₂) with flow rate of 1.0 mL min⁻¹ was used as a carrier gas. For batch or static system, the different volumes of PTFE vials (parker) were purchased from Sigma, Germany.

2.2. Reagents and Materials

All chemicals were purchased from Merck, and Sigma Aldrich companies, Germany. The stock solution of benzene (ppm, mgL^{-1}) was prepared (0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 ppm) and placed on vials as calibration curve of benzene by HS-SPME-GC-FID procedure. Benzene solution (99.7%) was purchased from Sigma and then, the eight solutions of benzene as standard calibration were prepared before proposed procedure. The other chemicals such as HNO_3 , HCl, acetone, methanol and ethanol with high purity (99%, GC grade) were purchased from Merck (Germany). The sorbent of NAC was synthesized by RIPI Nano laboratory. The NAC (≈ 50 nm), with 80% purity were synthesized. The characterizations of NAC were achieved by different spectra such as XRD, SEM and TEM. Ionic liquid (3-triphenylphosphonio-propane-1-sulfonate; $\text{C}_{21}\text{H}_{21}\text{O}_3\text{PS}$; CAS N: 116154-22-4, MW:384.43, 5 g) Was purchased from Sigma Aldrich, Germany (Fig. 1).

2.3. Synthesis of Nano activated carbon (NAC)

Activated carbons (ACs) was synthesized by the carbonized method for 2.0 h at 600 °C by activating at 900 °C in a furnace. The carbonized chars were followed by typically heats biomass feedstock in a kiln (pyrolysis) at temperatures between 300-800°C by Ar gas. The produced material was also known as charcoal (porous). Firstly, 20 g of raw powders prepared and placed in the porcelain crucible, then was heated up to 600°C per minute and hold for 2.0 hours. By decreasing temperature up to 25°C, the product is ready for weight. The activation of ACs based on microwave heating method caused to create the Nano activated carbon (NAC) by previous works. First, the carbonized sample was mixed with KOH (CS/KOH; ratio 1:3; wt/wt). By heating, the NAC was carried out at 800 °C (rate: 25 °C/min; hold: 1h) in a tube furnace and cooling down to room temperature under N_2 flow rate (0.5 Lmin^{-1}) [25,26].

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on a Seifert TT 3000 diffractometer (Ahrensburg, Germany) using nickel filtered $\text{Cu-K}\alpha$ radiation of wavelength 0.1541 nm. The textural properties of the sorbent including surface area, pore volume, and pore size distribution were determined by nitrogen adsorption-desorption isotherms using BELSORP-mini porosimeter (Bell Japan, Inc.). Prior to analysis, the samples were degassed under vacuum at 300 °C for 4 hours until a stable vacuum of 0.1 Pa was reached. The specific surface areas and pore volume of the sorbents were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The BET surface area of NAC was determined using a Micrometrics ASAP 2010 system. Scanning electron microscopy (SEM, Phillips, PW3710, Netherland) was used for surface image analysis of the sorbents. The morphology of sorbent was examined by transmission electron microscopy (TEM, CM30, Philips, Netherland).

2.5. Benzene Extraction Procedure

By procedure, 10 mg of NAC and 0.1 g of ionic liquid in 0.5 mL of acetone were mixed in glass tube. Then FSF was put into mixture and temperature increased up to 55°C. After vaporization of acetone, the NAC/IL was coated on FSF/SPME holder. When the probe of NAC-IL-FSF/SPME fixed in head space of GC vial, 1 g of powder samples (soil, vegetables) were placed in the bottom of vial and were closed in glass vial, tightly. The temperature of vial was increased up to 80°C by heat power accessory and benzene in soil and vegetables samples which were vaped/adsorbed by NAC/IL-SPME in head space of vial for 10 min. Then, the probe of NAC/IL introduced to injector of GC and benzene was determined by GC-FID (Fig. 1). The temperatures of GC injector and detector were tuned up to 200°C and 240°C, respectively. The temperature programming of oven was adjusted between 50- 220°C for 20 min. Based on results, benzene can be efficiently absorbed on the NAC/IL adsorbents with high recovery of more than 95%. The concentration of benzene according to the calibration curve was calculated and evaluated.

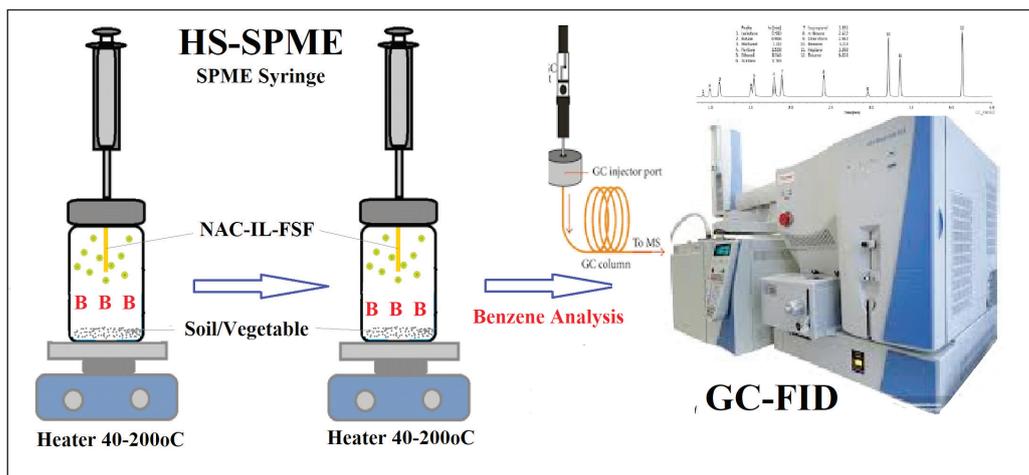


Fig.1. The procedure of benzene extraction in soil and vegetables samples based on NAC-IL-FSF/SPME by HS-SPME/GC-FID

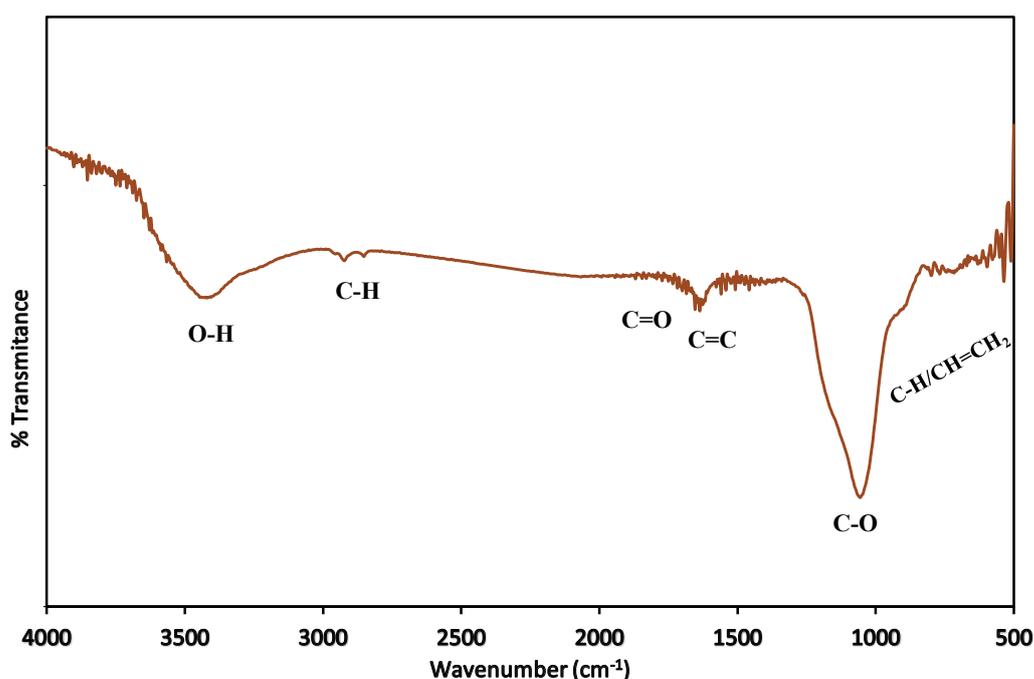


Fig.2. The FTIR spectrum of NAC

3. Results and Discussion

3.1. FTIR of ACNPs

The FTIR spectrum of NAC was shown in Figure 2. The band at 3430 cm^{-1} was related to the stretching vibration of OH group. The band at 2909 cm^{-1} and 2839 cm^{-1} were related to asymmetric and symmetric C–H stretching vibration of CH_2 bond.

The C=O stretching of COOH group shown in Figure 2 at 1710 cm^{-1} bond and peak at 1058 cm^{-1} was related to the C–O vibration mode. The peak at 1613 cm^{-1} belonged to C=C bond in benzene rings which was characterized by stretching vibration. The bands from 500 cm^{-1} to 850 cm^{-1} belonged to C-H and CH=CH₂ vibrations in aromatic rings.

3.2. SEM and TEM of NAC

FE-SEM and HR-TEM were used for morphological study of prepared NAC. The FE-SEM images of the synthesized NAC sample was shown in Figure 3. The FE-SEM images of NAC sample displayed small broken pieces of particles with irregular shapes, which can significantly affect the pore characteristics (e.g., pore size distribution and average pore diameter, Fig.3a). The NAC appeared to have many different sizes of pores, indicating that the structure had been destroyed and a dense porosity was formed through KOH activation. In order to observe the structure of NAC adsorbents, HR-TEM imaging was used. The HR-TEM image (Fig.3b) clearly shows the graphene-like structure with a 2D morphology, and the image with 50 nm scale confirms the existence of intermittent graphitic layers and porous structure.

3.3. Optimization of benzene extraction

All effected parameters such as the sorbent mass, amount of sample, the temperature, kind of ionic liquid, and time interaction were optimized in glass vials by static procedures. The benzene vapor was absorbed/extracted from 1 g of soil and vegetables samples with NAC-IL-FSF/SPME prob.

3.3.1. The effect of NAC and IL amount

As high extraction, the amount of NAC and IL coated on FSF has been optimized for benzene concentration between 0.1- 3.0 mg g⁻¹. Therefore, 2-25 mg of NAC and 0.02-0.2 g of ionic liquid in 0.5 mL of acetone were coated on FSF for benzene extraction in food, vegetable, and soil samples by the HS-SPME procedure which was coupled to GC-FID. The results showed the high recovery for soil/food /vegetable samples were obtained by 8 mg of NAC and 80 mg of ionic liquid for benzene adsorption by purposed procedure. So, 10 mg of NAC and 100 mg of ionic liquid coated on SFS was used for further work (Fig.4). The extra amount of NAC and ionic liquid had no effect on the extraction/adsorption efficiency of benzene from soil, food and vegetable samples.

3.3.2. The effect of temperature

The temperature is the main parameter for adsorption and desorption benzene from adsorbent by HS-SPME/GC-FID. The results showed the best adsorption of benzene from 1 g of powder soil and vegetables was achieved at 60-80°C in batch system for 10 min. After 10 min, extra time had no effect on the adsorption efficiency of benzene by NAC-IL-FSF. Also, increasing temperature more than 80°C caused to reduce adsorption efficiency by NAC/

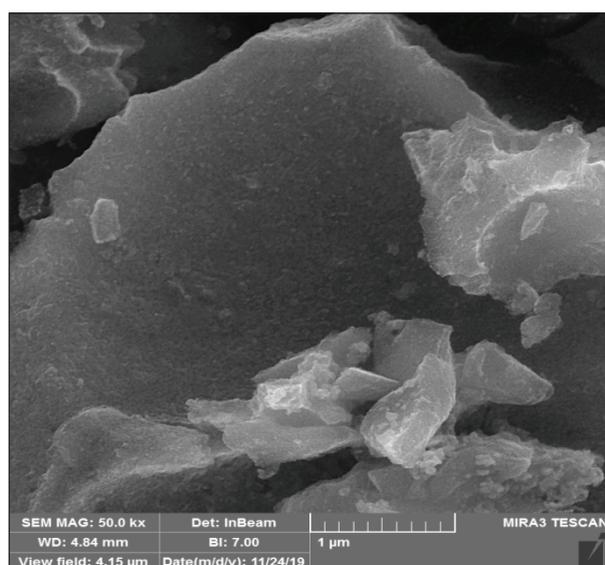


Fig.3a. The FE-SEM images of NAC sample

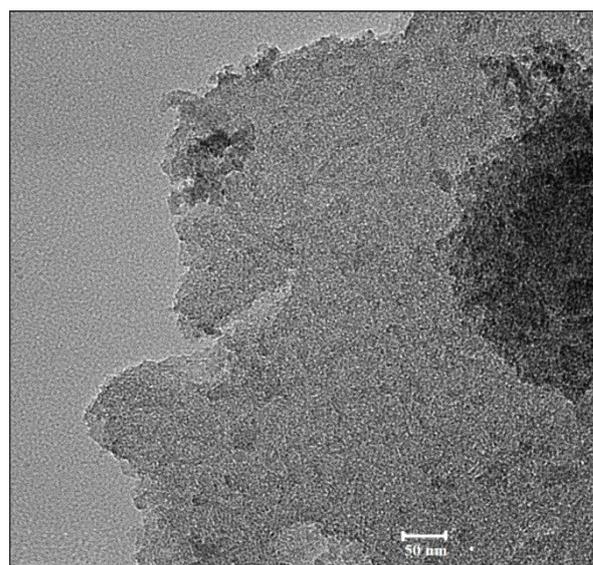


Fig.3b. The HR-TEM images of NAC sample

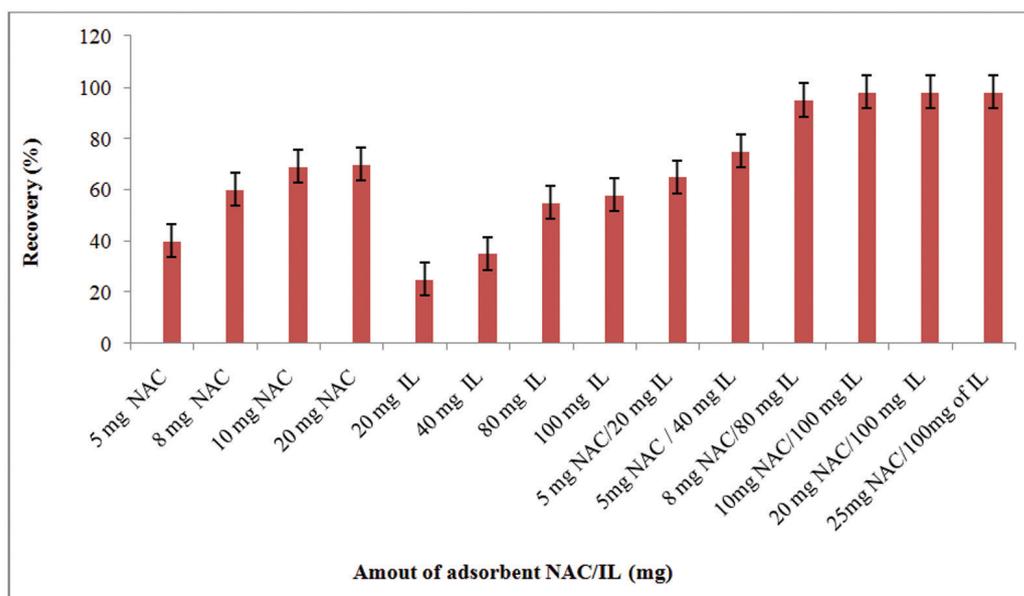


Fig. 4. The effect of NAC- IL amount for benzene extraction based on NAC-IL-FSF/SPME in soil/food /vegetable samples by HS-SPME/GC-FID

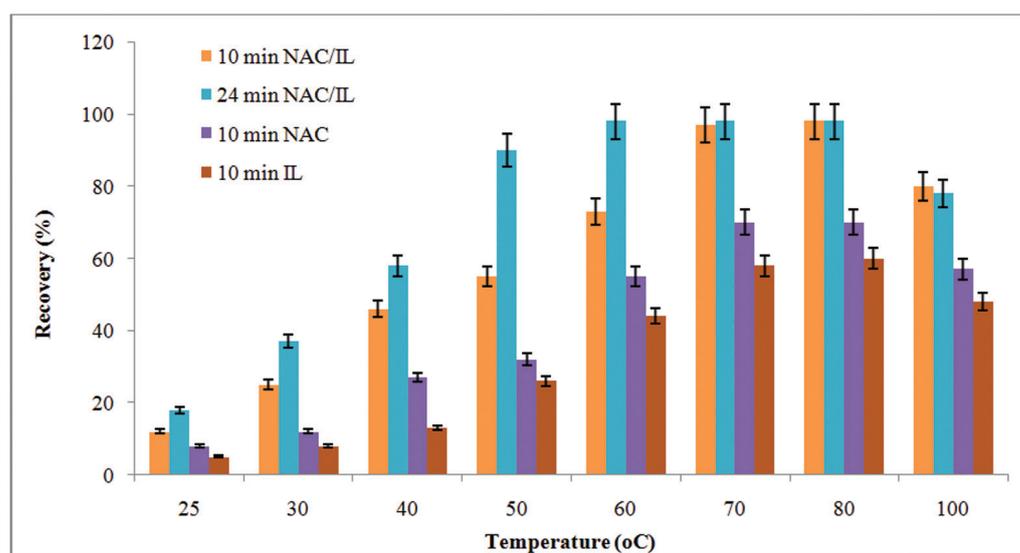


Fig. 5. The effect of temperature for benzene extraction in soil/vegetable samples based on NAC-IL-FSF/SPME by HS-SPME/GC-FID

IL. So, 70°C was selected as optimum temperature for benzene adsorption by NAC/IL in batch system (Fig. 5). Moreover, the adsorbed benzene on NAC-IL-FSF based on HS-SPME can be desorbed in injector of GC-FID at 200°C in presence of N₂ or Ar gas. The temperature programming of oven was adjusted between 50-220°C for 20 min. The results showed that by decreasing temperature less than 60°C, the recovery decreased up to 72.2% for 10 min and increased more than 95% for 24 min. In addition, after vaporization benzene in vial air hold for 2-3 min at 70-80°C and

then the temperature in batch system reduced up to 50°C for 7 min. Finally, the absorbed benzene on SFS probe was desorbed and determined by introducing to injector of GC-FID. The extraction efficiency and the absorption capacity of NAC/IL were obtained more than 95% and 127.2 mg g⁻¹, respectively. The results showed that the absorption capacity of NAC and IL were separately achieved at 72.6 mg g⁻¹ and 58.3 mg g⁻¹, respectively. So, in dynamic system, the values depended on flow rate of gas which was lower than batch system and must be optimized.

3.3.3. The effect of reaction time

Due to boiling point of benzene and vaporization at low temperature, it can adsorb on NAC/IL adsorbent in different time. The results showed that at low and favorite temperature the reaction time between benzene and adsorbent decreased and increased, respectively. By optimization, the minimum time for efficient recovery was obtained for 10 min at 70-80°C. When, the temperature reduced up to 50°C, all of benzene mass can be adsorbed on NAC/IL at 24.5 min. Therefor the reaction time depended on π - π interaction in aromatic chain of IL or NAC and physical adsorption of NAC. On the other hand, there is relationship between temperature and π - π interaction and best recovery was obtained for 10 min at 70-80°C.

3.3.4. The effect of different ionic liquids

The effect of different ionic liquids for benzene extraction from soil and vegetables was evaluated. So, the different ionic liquids such as [EMIM][PF6], [BMIM][PF6], [HMIM][BF4] and [PPP][S] as (3-triphenylphosphonio-propane-1-sulfonate; C₂₁H₂₁O₃PS) were mixed with NAC and dilution diluted with 0.5 mL of acetone. Then, the acetone was vaped at 55°C and IL/NAC were coated on fused silica fiber of SPME holder (NAC-

IL-FSF/SPME). The adsorbent was used for benzene extraction by HS-SPME/GC-FID. The results showed that the tri-phenyl of [PPP][S] with power π - π interaction of aromatic chain and different mass has more interaction with benzene aromatic cycles as compared to imidazolium rings in [EMIM][PF6], [BMIM][PF6] and [HMIM][BF4]. Therefore, [PPP][S]/NAC with ratio of 100 mg/10 mg was used for further work in optimized conditions which was shown in Figure 6.

3.3.5. Validation in real samples

The validation of HS-SPME/GC-FID method based on NAC-FSF/SPME and NAC-IL-FSF/SPME is important factor for extraction of benzene from soil and vegetables. By procedure, 0.1-3 mg L⁻¹ of benzene concentration was used for validation of methodology and the probe of SPME fixed in head space of GC vial. The 25 number of soil, vegetables powders (rice, cabbage, spinach) and standard solution of benzene were placed in the bottom of vial and were closed in the glass vial, tightly. All samples were validated by spiking of real samples with standard solutions based on NAC/IL-FSF/SPME probe by HS-SPME/GC-FID (Table 1 and 2). Finally, extraction efficiency was calculated by

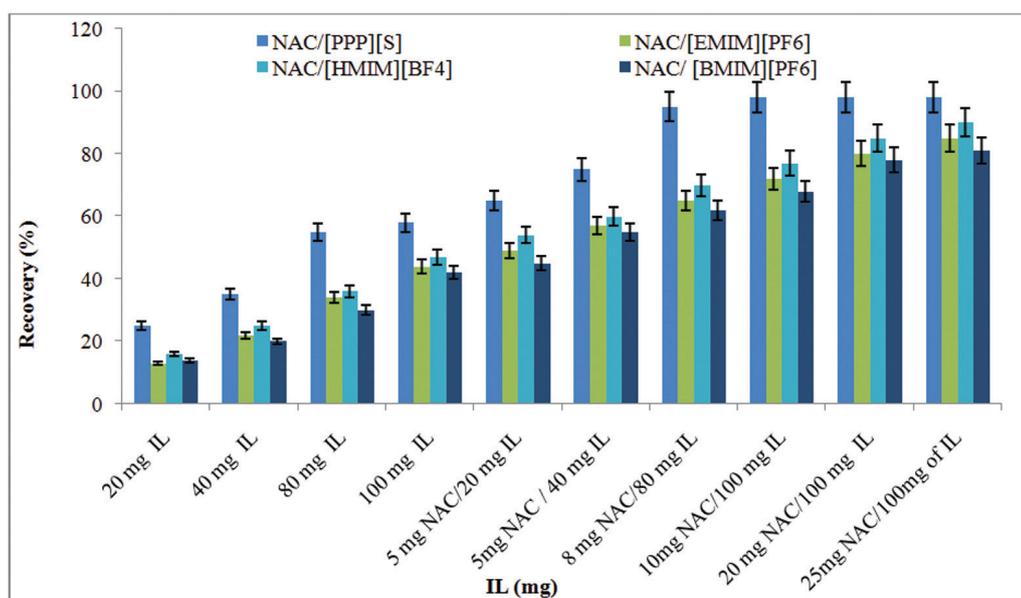


Fig. 6. The effect of different ionic liquids for benzene extraction in soil/food /vegetable samples based on NAC-IL-FSF/SPME by HS-SPME/GC-FID

Table 1. Validation of HS-SPME/GC-FID method based on NAC/IL-FSF/SPME for benzene extraction from soil and vegetables (1 g) near chemical industry

Samples	Benzene std. (mg L ⁻¹)	*Found Method (mg L ⁻¹)	Recovery (%)
A-Soil	----	2.45 ± 0.09	----
	2.0	4.40 ± 0.23	97.5
B-Rice	----	0.84 ± 0.05	----
	0.5	1.35 ± 0.06	102.2
C-Cabbage	----	1.32 ± 0.07	----
	1.0	2.28 ± 0.13	96.0
D-Spinach	----	0.76 ± 0.04	----
	0.5	1.24 ± 0.07	95.8
E-Eucalyptus	----	1.85 ± 0.11	----
	2.0	2.83 ± 0.14	98.3

* Mean of three determinations ± confidence interval (P = 0.95, n = 5)

Table 2. Validation of HS-SPME/GC-FID method based on NAC-FSF/SPME for benzene extraction from soil and vegetables (1 g) near chemical industry

Samples	Benzene std. (mg L ⁻¹)	*Found Method (mg L ⁻¹)	Recovery (%)
A-Soil	----	1.72 ± 0.08	----
	1.5	3.19 ± 0.16	98.2
B-Rice	----	0.59 ± 0.03	----
	0.5	1.07 ± 0.05	96.0
C-Cabbage	----	0.91 ± 0.06	----
	1.0	1.93 ± 0.12	102
D-Spinach	----	0.52 ± 0.03	----
	0.5	1.01 ± 0.07	98.0
E-Eucalyptus	----	1.27 ± 0.12	----
	1.5	2.83 ± 0.14	98.3

* Mean of three determinations ± confidence interval (P = 0.95, n = 5)

determining of benzene concentration by GC-FID in soil and vegetables. The efficient recovery of spiked samples had satisfactorily results with high accuracy and precision, which indicated the ability of HS-SPME/GC-FID method based on NAC/IL-FSF/SPME adsorbent for benzene extraction from

environmental samples. After desorption of benzene from NAC/IL-FSF/SPME probe in GC injector, the concentration of benzene was simply determined by GC-FID. For validation, the results based on NAC/IL-FSF/SPME probe with GC-FID were compared to high resolution GC-MS (Table 3).

Table 3. Comparing of proposed procedure with GC-MS based on NAC/IL-FSF/SPME for benzene extraction from soil and vegetables (1.0 g) near chemical industry

Samples	GC-MS (mg L ⁻¹)	*Found Method (mg L ⁻¹)	Recovery (%)
A-Soil	2.52 ± 0.08	2.42 ± 0.12	96.1
B-Rice	0.81 ± 0.04	0.83 ± 0.06	102.4
C-Cabbage	1.35 ± 0.06	1.34 ± 0.07	99.3
D-Spinach	0.80 ± 0.03	0.76 ± 0.05	95.0
E-Eucalyptus	1.88 ± 0.08	1.83 ± 0.13	97.3

* Mean of three determinations ± confidence interval (P = 0.95, n = 5)

4. Conclusions

In this study, NAC/IL-FSF/SPME as a new adsorbent was used for benzene extraction from soil, and vegetables powders by HS-SPME/GC-FID procedure. Based on results, the simple, fast, sensitive and accurate results based on NAC/IL adsorbent were demonstrated. The absorption of benzene based on NAC/IL-FSF/SPME probe had efficient recovery in the optimized conditions (more than 95%). The parameters such as the amount of NAC/IL, the amount of soil and vegetables, the temperature, kind of ionic liquid, and time were studied. In optimized conditions, the maximum adsorption capacity of 127.2 mg g⁻¹, 72.6 mg g⁻¹ and 58.3 mg g⁻¹ for NAC/IL, NAC and IL were obtained respectively, by HS-SPME/GC-FID. The results showed that the activity and reaction of NAC/IL for benzene extraction from soil/vegetables samples were more than NAC and IL in optimized conditions. Therefore, the applied and efficient procedure based on NAC/IL-FSF/SPME probe was used for extraction of benzene in environmental samples.

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