



Extraction and determination of benzene from waters and wastewater samples based on functionalized carbon nanotubes by static head space gas chromatography mass spectrometry

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ABSTRACT

Removal of benzene, as hazardous pollutants from waters and wastewater is a main problem of environment contamination due to high risk factor in human health. In this study, the phenyl sulfonic acid (PhSA) modified carbon nanotubes (CNTs) were used for benzene removal from waters by dispersive micro solid phase extraction method (D- μ SPE). Due to adsorption mechanism, the polar- π and π - π electron donor-acceptor interactions was provided between the aromatic ring of benzene with the surface sulfonic acid groups (SO_3H) and phenyl ring ($-\text{C}_6\text{H}_5$) of CNTs, respectively. Therefore, 20-100 mg of sorbent, concentration of benzene (0.1 – 10 mg L^{-1}), pH (1 – 12) and contact time (5 – 120 min) were investigated and optimized for benzene removal from water samples in static system. The concentration of benzene in water was determined by static head space gas chromatography mass spectrometry (SHS-GC-MS). The results showed, the Langmuir-Freundlich (LF) isotherm provided the best fit for benzene sorption. By using the Langmuir model, the maximum adsorption capacity of 157.34 mg g^{-1} and 22.86 mg g^{-1} was achieved for benzene removal from waters with CNTs@PhSA and CNTs, respectively. The method was validated by certified reference material in waters.

1. Introduction

Benzene is a chemical aromatic and flammable compound which is a natural component of petroleum-derived products. It is one of the most highly used groups of raw materials and solvents in numerous chemical synthesis processes, and manufacturing industries [1-3]. The presence of benzene in groundwater is due to petroleum product's leakage into water sources and leaking underground storage tanks and pipelines [4, 5]. According to the US Environmental Protection

Agency (EPA), benzene is one of the primary pollutants that adversely affects human health [6]. It is a serious health problem, causing several human diseases such as cancer, central nervous system disorders, leukemia, respiratory problems, skin and eye diseases [7-9]. Considering these health concerns and based on U.S.EPA announcement, the standard level of benzene in drinking water should not exceed $5 \mu\text{g L}^{-1}$ [6]. Therefore, it is crucial to remove this pollutant from water supplies, especially surface water, and ground waters. Since their discovery by Iijima et al in 1991 [10], Carbon nanotubes (CNTs) have been in a major area of

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interest within many contexts, especially in water treatment. CNTs are graphitic carbon sheets folded into hollow cylinders with diameters and lengths in nanometer and micrometer scales, respectively [11-13]. Unique properties of CNTs including hydrophobicity, high specific surface area, hollow and layered structure and existence of π -electrons on their surface make them superior adsorbents for removal of contaminants [14-16]. Some studies put further steps and investigated the effect of CNT's modification on their adsorption performance. Lu et al. showed that NaOCl-oxidized CNTs have significant adsorption capacity in comparison to other types of carbon adsorbents [17]. Su et al conducted a research in which multiwalled carbon nanotubes were oxidized by sodium hypochlorite solution and turned to a new adsorbent with enhanced adsorption performance [18]. These studies show high affinity of CNTs toward organic compounds, and open new avenue for developing carbon nanotube technologies to treat benzene and other organic chemicals in water. However, there is a high number of CNTs that can be used to remove benzene from water supplies and which subtype of CNTs family can have the most effective adsorption capacity, is still unknown. To our knowledge, so far, there is no data about the adsorption capacity of *phenyl* sulfonic acid (PhSA) modified hybrid carbon nanotubes (CNTs). Therefore, the main objective of this study is using *phenyl* sulfonic acid (PhSA) modified hybrid carbon nanotubes (CNTs) to remove benzene from water sources by dispersive solid phase extraction method.

2. Experimental

2.1. Material and methods

Gas chromatography based on mass detector (GC-MS) and air sample loop injection (ASL) was used for benzene determination by static head space accessory (SHS-GC-MS, Netherland). The headspace may be sampled using a gas tight syringe of appropriate volume. Gas-tight syringe (GTS) was used for determination VOCs¹ from water samples by shaking and heating samples.

1- Volatile organic compound

The auto-sampling of GTS units can retrofit to a standard GC with a split/split less injector. The GTS auto-sampler is beneficial for use with diverse samples. The Agilent 7890A GC can accommodate up to three detectors identified as front detector, back detector, and auxiliary detector. This model of GC design with three detectors in front, back, and auxiliary (FID, TCD, MS) and equipped with a split injector with poly di-methyl siloxane column (Table 1). The mass detector chosen was selected for benzene analysis in gas/liquid. Before injection, Slide the plunger carrier down until it is completely over the syringe plunger, and tighten the plunger thumb screw until finger-tight. The injector temperature was adjusted to 190°C and the detector temperature at 240°C. The GC oven temperature was programmed from 25°C to 250°C which was held for 12 min. Hydrogen (Cas number: 1333-74-0) as the carrier gas was used at a flow rate of 1.0 mL min⁻¹. The scanning electron microscopy (SEM) and Raman spectra were recorded by electron microscopy and spectrometer of CNTs@PhSA (Bruker). Fourier transformed infrared spectroscopy (FTIR, IR-200 Thermo-Nicolet 2.2) in KBr in the range 400–4000 cm⁻¹ was used to confirm the covalently bound benzenesulfonic acid (CAS N: 98-11-3) group on the CNT surface. Transmission electron microscopy (TEM, Philips) with a conventional 15 kV electron microscope was used to analyze the surface morphology of CNTs@PhSA. X-ray diffraction (XRD; Panalytical) was used for XED patterns with wavelength 0.15405 nm for CNTs@PhSA. The intensity was measured by step scanning in a 2 θ range of 5–80°. Benzene (CAS N: 71-43-2; C₆H₆) purchased from Sigma Aldrich. Five calibration solutions of benzene were prepared and the approximate concentrations of benzene were 0.1, 0.2, 0.5, 1.0, 5.0 and 10 mg L⁻¹. The other chemicals with high purity (99%) were purchased from Sigma (Germany). The analytical grade solvents such as benzene, chloroform, (CAS N: 67-66-3), 4-benzenediazoniumsulfonate (CAS: 305-80-6), acetone (CAS N: 67-64-1), HNO₃ (CAS N: 7697-37-2), HCl (CAS N: 7647-01-0), H₂SO₄ (CAS N: 7664-93-9), acetic acid (CAS N:

64-19-7) and NaOH (CAS N:1310-73-2) were also from Merck. CNTs@PhSA was synthesized in RIPI laboratory, Iran. Ultrapure water (18 MΩ·cm) was obtained from Millipore continental water system (Millipore, USA). Samples of water and wastewater collected in polyethylene bottles were filtered through Millipore cellulose membrane filter (0.45 μm porosity) to remove suspended particulate matter.

2.2. Synthesis of phenyl sulfonic acid modified hybrid carbon nanotubes

High-purity CNTs were synthesized by use of camphor, an environmentally friendly hydrocarbon as a carbon source using chemical vapor deposition method on Co–Mo/MgO nanocatalysts. The nanocatalyst was synthesized by sol-gel method. HCNTs were grown at temperatures of about 900–1000°C in 45–60 min. Concentration of active metals was 5–10%. The nanocatalyst (Co–Mo/MgO) was prepared by our special sol-gel method [19]. For functionalization of CNTs with phenyl-SO₃H (CAS N: 98-11-3) group, CNTs surface was activated by 50% HNO₃ (CAS N: 7697-37-2) for 1 h and washed with ultrapure water many times. The diazotization reaction was used for functionalization as follows; 0.03 mol of sulfanilic acid CAS N: 121-57-3) was dispersed in 300 mL of 1 M HCl (7647-01-0) in a three-necked ground flask [20]. The flask was kept in an ice water bath and the temperature controlled around 3°C under stirring. Then, 33 mL of 1 M NaNO₂ (CAS N: 7632-00-0) was added dropwise into the mixture and stirred for 1 h at the same temperature. The resulting precipitate was filtered and washed

Table 1. The conditions of GC-MS for determination benzene

GC-MS	Conditions
Model	Agilent, 7890A
Sensitivity	0.1-20 ng
Injection Volume	1-5 μL; 10:1 split
Split ratio	2:1
Column	30 meter, 0.32mm x 0.25μm
Temperature Injector	220 °C
Detector FID	230 °C
Program , time= 5.0 min	25 to 100 °C at 25 °C per min
Carrier Gas	N ₂ , 1 mL min ⁻¹
Column Oven Pressure	60°C
Pulse	
Column Flow	6 ml min ⁻¹
Retention Time	8.153 (min)
Run Time (Min)	19.125 (min)
Flow Rate N ₂	30 (mL min ⁻¹)
Flow Rate H ₂	34(mL min ⁻¹)
Injection size	1-5μL
Flow Rate air	200-400(mL min ⁻¹)

with deionized water. In the following step, 5 g of 4-benzenediazonium sulfonate and 180 mg of activated CNTs were added into 120 mL of mixture of water and ethanol (1:1, v/v) at 3°C. Subsequently, 60 mL of H₃PO₂ aqueous solution (50 wt.%) was added to the mixture and stirred for 30 min. After this time, another 60 mL of H₃PO₂ (CAS N: 6303-21-5) was added and stirred for 1 h. The resulting mixture was washed with deionized water and dried overnight in an oven at 80°C (Fig. 1).

2.3 Extraction Procedure

The CNTs@PhSA nanostructures based on D-μSPE method was used for extraction of benzene from waters (Fig. 2). First, 10 mg of CNTs@PhSA or

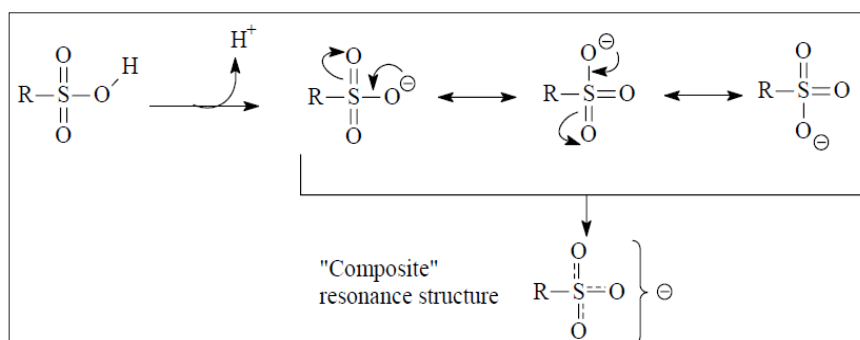


Fig. 1. Synthesis of composite with resonance structure

CNTs nanostructures was put on 5 mL of water samples with different benzene standard solution ($0.1\text{--}10\text{ mg L}^{-1}$) in GC vial. The mixture shaken for 10 min by magnetic shaker accessory (MSA) and after centrifuging for 3 min (3500rpm), the solid phase separated from liquid phase and finally the benzene concentration in water sample was determined by static head space gas chromatography mass spectrometry (SHS-GC-MS). After extraction, the recoveries were calculated with the ratio of initial/final concentration of benzene in vial GC by SHS-GC-MS (Eq. A). In addition, adsorption capacity and removal efficiency (RE) was calculated by equation Eq. B and Eq. C. X is the initial concentration of benzene in solution and Y is final concentration of benzene which determine by SHS-GC-MS in water samples. The adsorption capacity (AC) of benzene (mg g^{-1}) and, the removal efficiency of benzene (%) was shown in Eq. B and Eq. C. The C_i (mg L^{-1}) and C_f (mg L^{-1}) are the concentration of benzene before and after extraction procedure, V_s (L) is the sample volume, and mass (g) is the amount of CNTs@PhSA.

$$R = \frac{X}{Y} \times 100 \quad (\text{Eq. A})$$

$$AC = \frac{(C_i - C_f) \times V_s}{\text{Mass}} \quad (\text{Eq. B})$$

$$RE (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (\text{Eq. C})$$

3. Results and discussion

Mechanism of extraction of benzene with CNTs@PhSO₃H was achieved based on π - π stacking between aromatic chain and S=O bond of CNTs@PhSO₃H and SO₃ b and molecular of benzene in waters by sandwich or T shaped π - π bonding (Fig. 3).

3.1. Characterization

Figure 4 (a, b) showed the SEM and TEM images revealed the CNTs@PhSO₃H consist of randomly aggregated and crumpled thin tubes which are closely associated with each other forming a disordered solid, and it can be inferred that the functionalization process does not change the general structure of HCNTs. The FTIR spectrum of the CNTs@PhSO₃H sample showed the O=S=O, OH as a broad peak, C=C and C-S bond which was confirmed the SO₃ bond in CNTs (Fig. 5). Raman spectroscopy is a useful technique for the characterization of carbon nanotubes quality. Raman patterns of CNTs@PhSO₃H confirm the presence of CNTs (Fig. 6) and XRD image showed the hexagonal structures in CNTs@PhSO₃H. After the attachment of SO₃H groups on the carbon wall of CNTs the three peaks which confirms the functionalization of SO₃H on CNTs@Ph have not any changes on the structure of CNTs (Fig. 7).

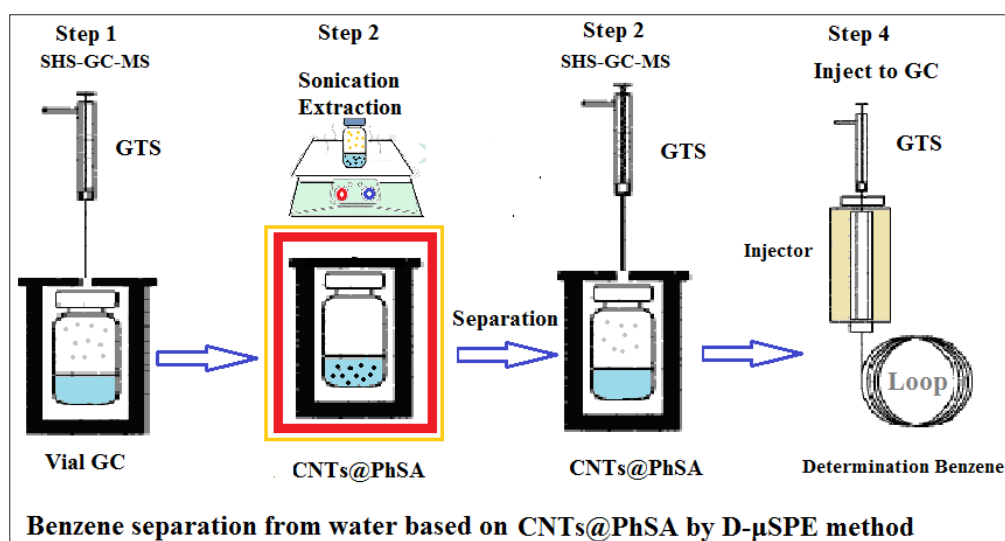


Fig. 2. Benzene extraction from waters based on CNTs@PhSA by D-μSPE method

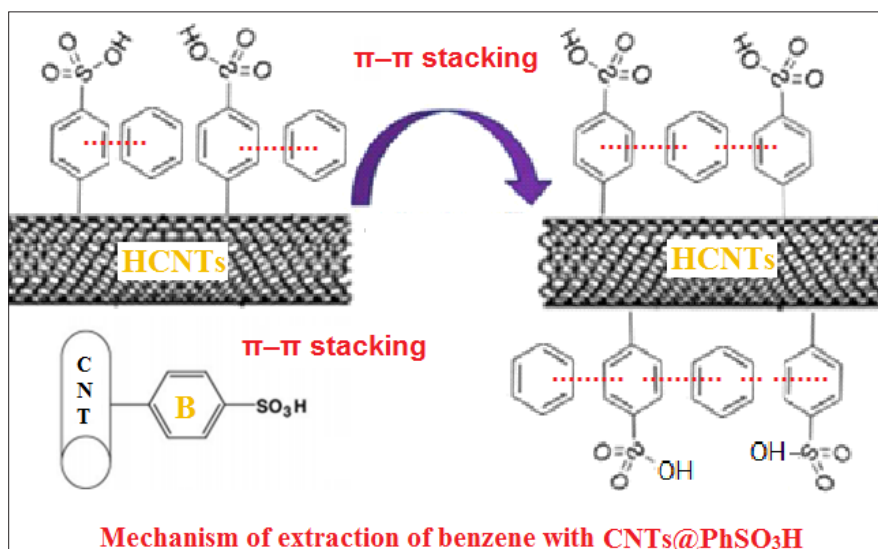


Fig. 3. Mechanism of extraction of benzene with CNTs@PhSO₃H

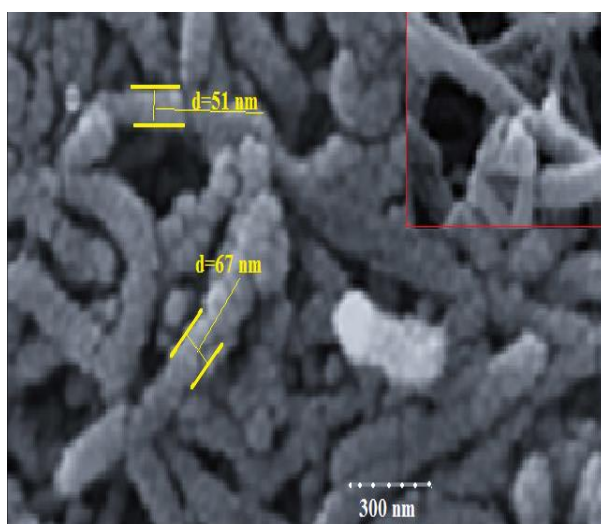


Fig. 4(a). SEM of CNTs@PhSO₃H

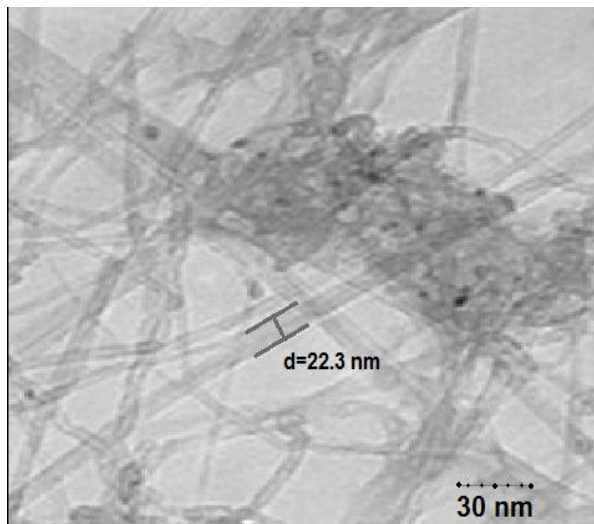


Fig. 4(b). TEM of CNTs@PhSO₃H

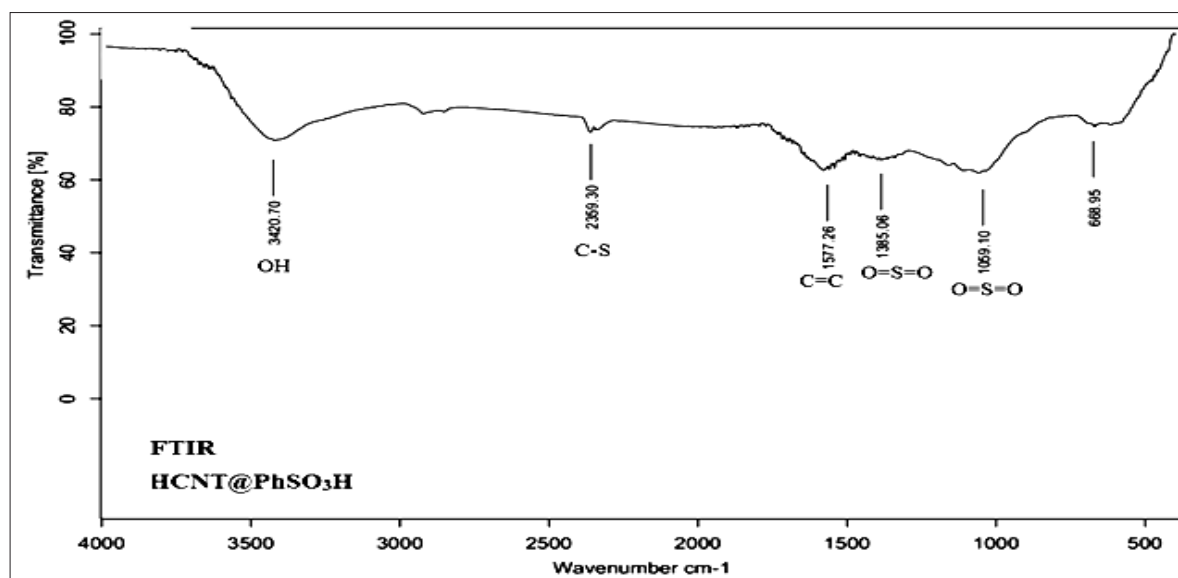


Fig. 5. FTIR spectrum of the CNTs@PhSO₃H

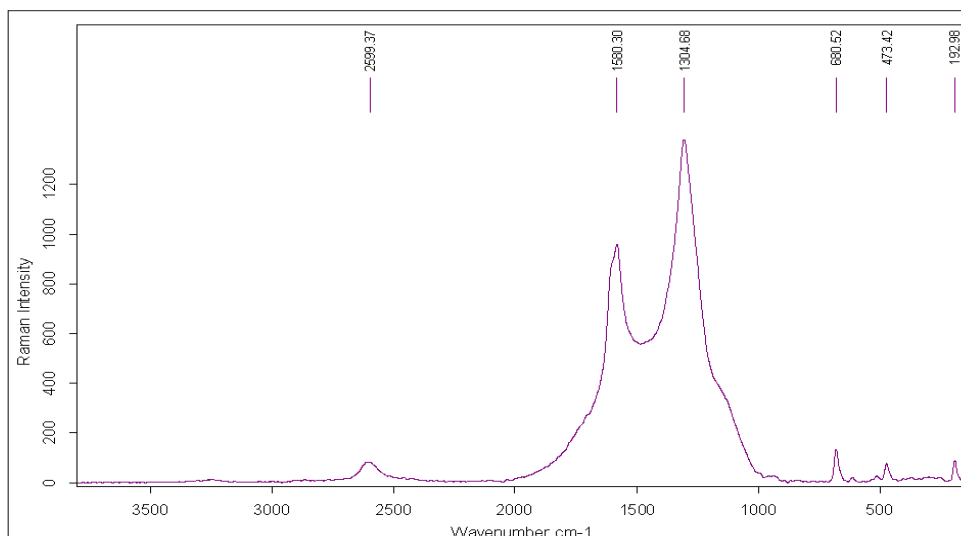


Fig. 6. Raman patterns of CNTs@PhSO₃H

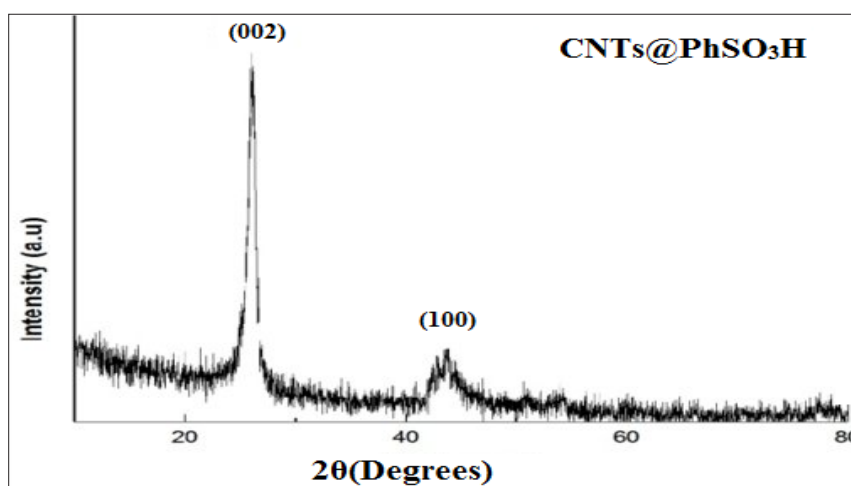


Fig. 7. XRD image of hexagonal structures in CNTs@PhSO₃H

3.2. Optimization parameters

The D- μ -SPE procedure based on CNTs@PhSO₃H nanocomposite was used for extraction of benzene from well water and wastewater samples. The main effectiveness parameters such as, pH, amount of CNTs@PhSO₃H, volume of waters, adsorption capacity of sorbent were evaluated and studied. The pH sample is critical parameters and must be optimized. High adsorption of benzene from water samples based on CNTs@PhSO₃H nanocomposite depended on pH solution which was extracted by D- μ -SPE methods. The pH range (1-12) was adjusted with buffer solution and the extraction efficiency of benzene in water samples was evaluated by benzene concentration (0.1-10 mg L⁻¹) and 10 mg of CNTs@PhSO₃H. The results

showed, the recovery of extraction for benzene was decreased at acidic and basic pH ranges. Therefore, pH of 5.5-7.5 was selected as optimized pH for benzene extraction in waters (Fig. 8).

By D- μ -SPE method, the amount of on CNTs@PhSO₃H nanocomposite was studied for 5 mL of water and wastewater samples. So, 1-20 mg of CNTs@PhSO₃H and CNTs was examined by proposed procedure. The results showed us, benzene in water samples can be efficiently extracted with 8 mg CNTs@PhSO₃H in optimized pH=7. So, 10 mg of CNTs@PhSO₃H nanocomposite was used as optimum mass for benzene extraction in waters (Fig. 9).

The sample volume (SV) in important factor and must be studied. So, the effect of sample

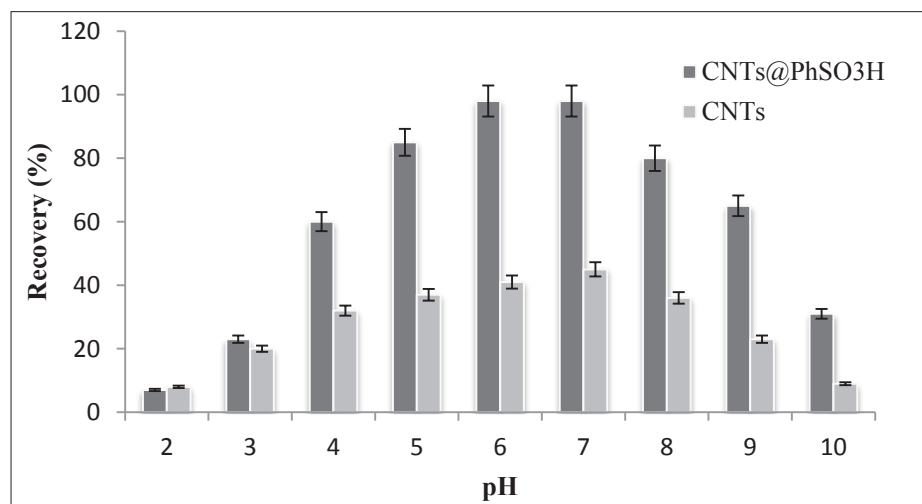


Fig. 8. The effect of pH on benzene extraction from water samples

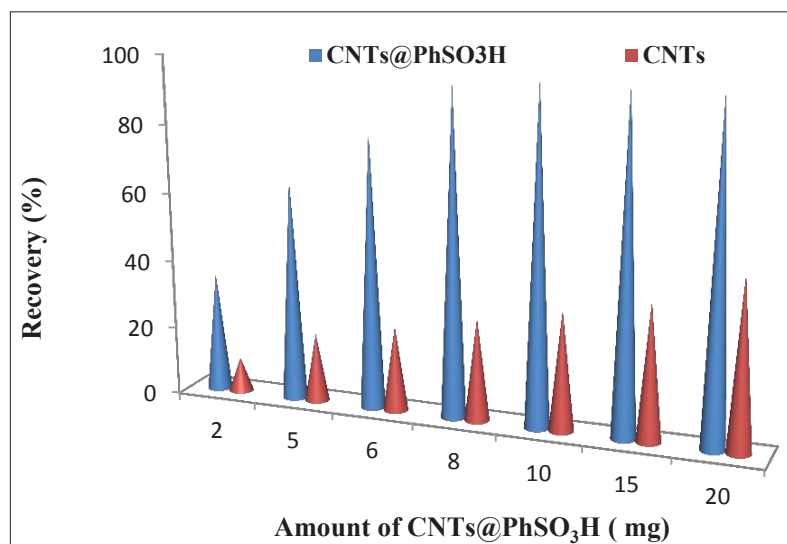


Fig. 9. The effect of amount of CNTs@PhSO₃H on benzene extraction by D-μ-SPE method

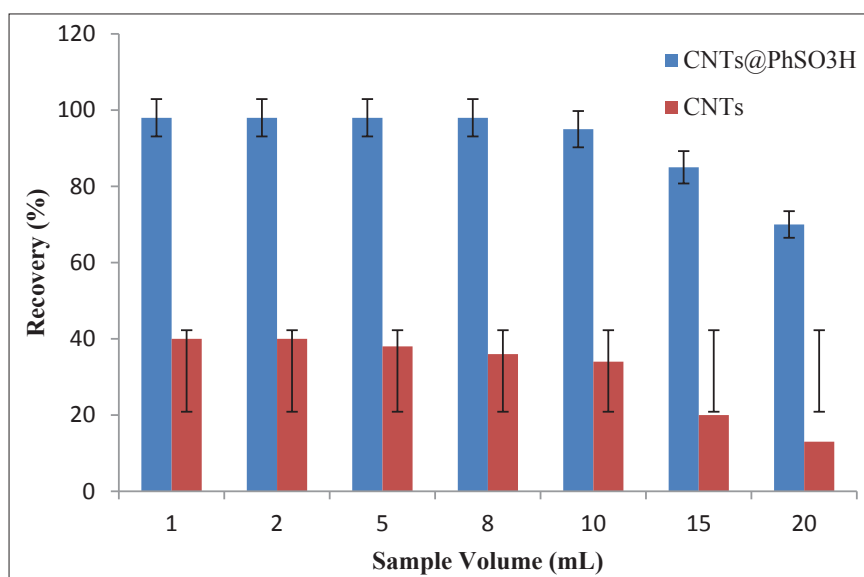


Fig 10. The effect of sample volume on benzene extraction by D-μ-SPE method

volume on benzene extraction in waters examined at optimized conditions. Due to procedure, the different water volumes between 1-10 mL with 10 mgL⁻¹ of standard benzene solution were selected for benzene extraction by D-μ-SPE methodology. As magnetic shaking for 10 min, high recovery obtained for 10 mL of waters. Therefore, 5 mL of sample volume selected for further work (Fig. 10).

The validation methodology based on spiking well water and wastewater samples was achieved by concentration of standard benzene solution from LLOQ as 0.1 mgL⁻¹ and ULOQ as 10 mgL⁻¹ by optimized conditions (Table 2). All samples analyzed by static head space gas chromatography mass spectrometry (SHS-GC-MS).

3.3. Discussion

This study set out with the aim of assessing the

modification of CNTs with phenyl sulfonic acid group and its effect on the extraction efficiency of benzene in water samples. According to our results, it is revealed that compared to CNTs, CNTs@PhSA significantly adsorbs benzene in water. As table 3, the results showed us the proposed method based on CNTs@PhSA had more efficient extraction of benzene from waters than CNTs sorbents which was presented by different authors [21-26]. Also the comparing of adsorption capacity(AC) of CNTs@PhSA (157.34 mg g⁻¹) with other sorbents such as CNTs (22.86 mg g⁻¹), CuO-NPs (100.24 mg g⁻¹), GO/MOF-5 (77 mg g⁻¹), ZIF-8/GO(123 mg g⁻¹) and GO (158 mg g⁻¹) showed, the value of AC was near or more than others [27-30]. Osanloo et al. used graphene modified by ionic liquid (NG-IL) for toluene removal [31].

Table 2. The validation methodology based on CNTs@PhSO₃H by SHS-GC-MS

samples	Added (mgL ⁻¹)	*Found (mgL ⁻¹)	Recovery (%)
Well Water	-----	0.43 ± 0.02	-----
	0.5	0.94 ± 0.03	102
Paint Wastewater	-----	14.16± 0.68	-----
	15	28.87± 1.26	98.1
Oil-Factory Wastewater	-----	38.12± 2.15	-----
	40	76.82± 3.75	96.8

* Mean of three determinations ± confidence interval (P = 0.95, n = 10)

Table 3. Comparing of dispersive micro solid phase extraction method based on CNTs@PhSA for benzene extraction from water samples with other published methods

This Study	Relevant Studies
In this study, phenyl sulfonic acid group was used for modification of CNTs in order to extract benzene from water samples.	CNTs have the capacity to be attached by functional groups. These functional groups can change physical and chemical properties of carbon nanotubes [21].
We prepared a range of benzene concentration including 0.1, 0.2, 0.5, 1.0, 5.0, 10 mg/L	Optimum benzene concentration for the investigation of CNTs adsorption efficiency in benzene removal procedure is 10 mg/L [22].
Contact time performed in this study was 10 min.	The mixture of CNTs and sample have been shaken for 10 minutes [22].
Extraction of benzene in waters by sandwich or T shaped π-π bonding.	Molecular torsion balance, developed by Wilcox et al. representing a closed model with a T-shaped π-π interaction [23, 24].
SEM and TEM images revealed that the CNTs@PhSO ₃ H consists of randomly aggregated and crumpled thin tubes.	CNTs accumulation leads to pores formation which can create a bunch of adsorption sites on them [25].
Addition of SO ₃ H on CNTs@Ph had no change on the structure of CNTs.	According to SEM images of H ₂ SO ₄ -treated CNTs, there is no change in the morphology and structure of CNTs [21].
pH optimization in the range of 5.5-7.5 benzene extraction from water samples	When pH exceeds 6.2, the adsorption efficiency increases significantly [26].

4. Conclusions

The main goal of the current study was to determine the effect of phenyl sulfonic acid group functionalization on the adsorption efficiency of CNTs for benzene removal in water samples. The adsorption mechanism is referred to the polar- π and π - π interaction between aromatic ring of benzene and surface sulfonic acid group as well as phenyl ring. Surprisingly, hexagonal structure of CNTs@PhSA indicated no change in the basic structure of CNTs, after functionalization with SO_3H . However, the adsorption capacity of CNTs@PhSA for benzene removal was significant. These findings suggest that in general, CNTs are capable of being modified and therefore, they represent a critical role in the adsorption of benzene and other pollutants. All concentration benzene in waters determined based on D- μ -SPE procedure by SHS-GC-MS. Under optimal conditions, adsorption efficiency of CNTs@PhSA and CNTs was obtained 97.7% and 20.6 % for benzene removal from water samples, respectively.

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