



Removal of benzene vapor from the air based on novel tantalum metal-organic framework (Ta-MOF) adsorbent by gas flow solid-phase interaction before determination by gas chromatography

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ABSTRACT

Benzene has a carcinogenic effect on the human body and adsorption from the air is the best way to control it. By this research, benzene vapor was removed from the air based on a tantalum metal-organic framework (Ta-MOF) by gas flow solid-phase interaction (GF-SPI). Benzene adsorption with Ta-MOF was studied in the static and dynamic systems at room temperature. The benzene concentration was analyzed by gas chromatography equipped with an FID detector (GC-FID). The factors affecting benzene removal efficiency like initial concentration of benzene, amount of adsorbent, exposure time, flow rate, and temperature were studied and optimized. The results showed us, the adsorption capacities range of Ta-MOF for benzene in the static and dynamic system were obtained between 90-160 mg g⁻¹ and 65-135 mg g⁻¹, respectively. Also, the high removal efficiency was achieved by more than 95% at 45°C, 67.5 mg L⁻¹ benzene concentration, 0.5 g of Ta-MOF, and the flow rate of 250 mL min⁻¹ for a dynamic system. By dynamic system, the benzene is generated in the chamber, stored in a bag, and then moved on the surface of Ta-MOF. The GF-SPI method was validated by GC-MS and spiking real samples.

1. Introduction

Volatile organic compounds (VOCs) contain a carbon structure with a high vapour pressure at room temperatures [1]. These compounds are known air pollutants released through industrial activities such as liquid fuels and cleaning supplies [2]. Benzene is a hazardous pollutant in the air that workers in various industries (oil and chemicals) exposure to it [3]. Benzene has been classified as a

definitive carcinogen in humans since 1979 based on sufficient evidence of leukemia. Benzene can replace by toluene or derivatives with less toxicity [4,5]. Benzene exists in fuels such as gasoline and is used in the production of styrene, dyes, inks and polymer products [6, 7]. Benzene enters into the air through different ways such as gasoline leakage, pipelines and petrochemical effluents[8]. Exposure to benzene can affect human health and cause cancer, CNS impairment, and kidney diseases [7, 9, 10]. The benzene is volatilized and distributed in air, soil, water and foods [11,12]. Exposure to BTEX products causes many problems in the

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human body [13-15]. By increasing stringent environmental standards, the actual control for the removal of VOCs is the principal aim [16]. Methods developed to control and remove VOCs emission on industrial plants including, condensation, adsorption, catalytic oxidation, and biodegradation methods. Whereas adsorption onto sorbents such as activated carbon, zeolites, and cotton fibres has been the reliable option so far [17,18]. Adsorption is one of the most efficient ways to control the emission of VOCs [19]. Some common adsorbents for the adsorption process are carbon quantum dots (CQDs), graphene (NG), resin, zeolite, and carbon nanotubes [20]. Metal-organic frameworks (MOFs) are relatively new compounds made of porous crystal materials and are being studied as adsorbents since 1998 [21]. These materials are regular polymers that are formed from different metals and bonds between metals created by organic compounds [22]. Organic-metal framework compounds use in clean energy, as the most important storage devices for gases such as hydrogen and methane, as well as high-capacity adsorbents to meet various separation needs [23]. The previous studies have shown that these adsorbents have excellent performance in absorbing benzene vapours. For instance, in 2008, Bright and colleagues studied benzene adsorption efficiency on various adsorbents made from MOFs. The adsorption occurs at the same conditions at 25°C and 440 ppm benzene concentration. Also, the adsorption capacities of the adsorbents varied from 2 to 176 mg g⁻¹. The MOF-199 sorbent had the highest absorption rate [24]. In 2019, Vikrant et al. Examined conventional adsorbents such as activated carbon for the adsorption of gaseous benzene compared to the new adsorbent of the metal-organic framework. The results showed the highest efficiency of MOF-199 was 94.8 mg g⁻¹, which was slightly higher than the other adsorbent, activated charcoal (93.5 mg g⁻¹). Also, the adsorption efficiency of the adsorbent MOF(UiO-66) is 27.1 mg g⁻¹, which is lower than the activated charcoal adsorption efficiency [25]. In 2011, Young and colleagues studied the adsorption of VOCs by

the metal-organic framework, MIL-101(Cr), influenced by the shape and size of the molecule and concluded that benzene adsorption capacity in MIL-101 was 1291±77 mg g⁻¹ [21]. Ahmaruzzaman and Xiang et al showed that activated carbon has desirable physical and chemical properties, which made it useful as an adsorbent and was used in the industry for decades. Sone et al were reported the CNTs can be used for BTEX removal from the air. They showed the carbon nanotubes are promising better absorbed than other carbon materials due to their unique properties. The CNT has been defined as cylindrical porous with walls made of crystalline graphite layers. Many technologies, such as bio-filter system [26], surface interaction [27], separation [28], adsorption [29, 30], and nanocatalyst [31], were used for VOCs removal. In addition, the various adsorbents such as activated carbon based on cellulose acetate [32], carbon nanotube (MWCNTs) [33], Zeolite [34], the graphene-modified by IL [35] were reported for removal benzene and BTX from the air.

In this study, benzene vapour was removed from the air based on a tantalum metal-organic framework (Ta-MOF) by the gas flow solid-phase interaction (GF-SPI). Benzene adsorption based on Ta-MOF was evaluated in the static and dynamic systems. The benzene concentration was analyzed by the GC-FID. The main parameters such as temperature, flow rate, the adsorbent mass and benzene concentration were optimized.

2. Material and Methods

2.1. Instrumental and reagents

All of the chemical compounds such as benzene anhydrous (99.8%, CAS N.: 71-43-2), tantalum chloride (CAS N: 7721-01-9 TaCl₅), benzene tetracarboxylic acid (CAS N.: 89-05-4), the cetyltrimethylammonium-Bromide (CAS N.: 57-09-0), and propane had high purity and were purchased from the Merck/Sigma company (Germany). Five calibration solutions of benzene were prepared. The approximate concentrations of benzene were prepared from 0.1, 0.5, 1.0, 1.5, and 2.0% (v/v). The other chemicals

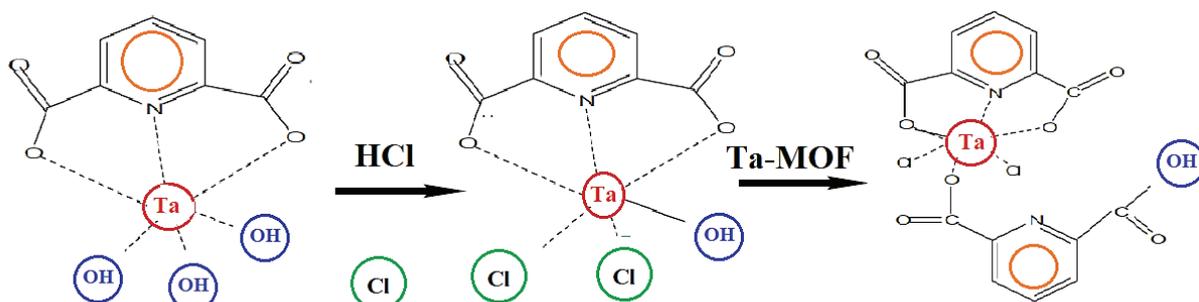


Fig.1. Preparation steps for synthesis of the tantalum metal-organic framework

based on GC grade and 99% purity were purchased from Merck (Germany). The characterization of the synthesized MOF was carried out via SEM-Philips XL 30, UK, and the X-ray diffraction equipment (XRD) Rigaku XDS 2000. The Agilent 7890A GC based on three detectors was used for benzene determination. The FID detector chosen was selected for benzene analysis in air. For injecting, slide the plunger carrier down and tighten the plunger thumb screw. Due to sampling valves, we introduce a sample of fixed size into the carrier gas stream. Valves are most frequently used to sample air or liquids. Gas sampling bags with valve and septum port (Tedlar) and air sampling apparatus (Bucket brigade) were prepared. The split/splitless injector, FID, and a column coated (50 m \times 0.2 mm id.) was used by GC. The injector temperature was adjusted to 200-210°C and the detector temperature at 240-250°C. The GC oven temperature was tuned at 220°C. Hydrogen as the carrier gas was used at a flow rate of 1.0 mL min⁻¹ with a split ratio of 1:100. Vials with PTFE air-tight cap (parker) were used as a batch/static system.

2.2. Preparation of the tantalum metal-organic framework

In this study, the MOF adsorbent was prepared by Rezaie and colleagues' research [36]. A solution of tantalum chloride (0.027 g) and benzene tetracarboxylic acid (0.011 g) was prepared in 17 mL double distilled water (DDW). The solution prepared from the reaction above and then added to the mixture of 0.77 g cetyltrimethylammonium-Bromide and 8 mL propane in a 50 mL Pyrex tube.

This new compound is then put in a microwave bath of 45°C and microwave bath with a power of 220 watts for 30 minutes. After 45 minutes of centrifuging, the MOF white crystals were formed, and then the product was left to dry in an argon atmosphere (Fig.1).

2.3. Benzene preparation in a dynamic system

First, the air was purified with an electro air cleaner (EA-HEPA600M) based on HEPA and activated carbon which was removed particles 200-300 nm (99.97%) and VOCs from the air, respectively. Then, the pure air passed through the chamber and entered to PVC bag (5 Li) by an SKC pump. The amount of H₂O (vapor) was controlled by adjusting the amount of water injection. All of the gas lines and bags were covered with heating jackets at 50-60 °C to prevent H₂O (vapor) and benzene from condensing (Fig.2).

2.4. Static and dynamic adsorption procedure

For the static experiment, 10 mL of different concentrations of benzene were drawn with a syringe and injected into the vials that were air-tightened with a PTFE lid and contained the Ta-MOF adsorbent. After a specific time, 100-500 microliter air from the vial was extracted and injected into the GC-FID analyzer for determining benzene. The effect of four exposures, times (5, 10, 15, and 20 minutes), the amount of Ta-MOF adsorbent in four amounts (0.5, 1, 1.5, and 2 mg), four different concentration levels (30, 50, 70, and 100 mg L⁻¹ of benzene) and, two temperatures of 25 and 45°C based on Ta-MOF adsorbent were studied (Fig.3).

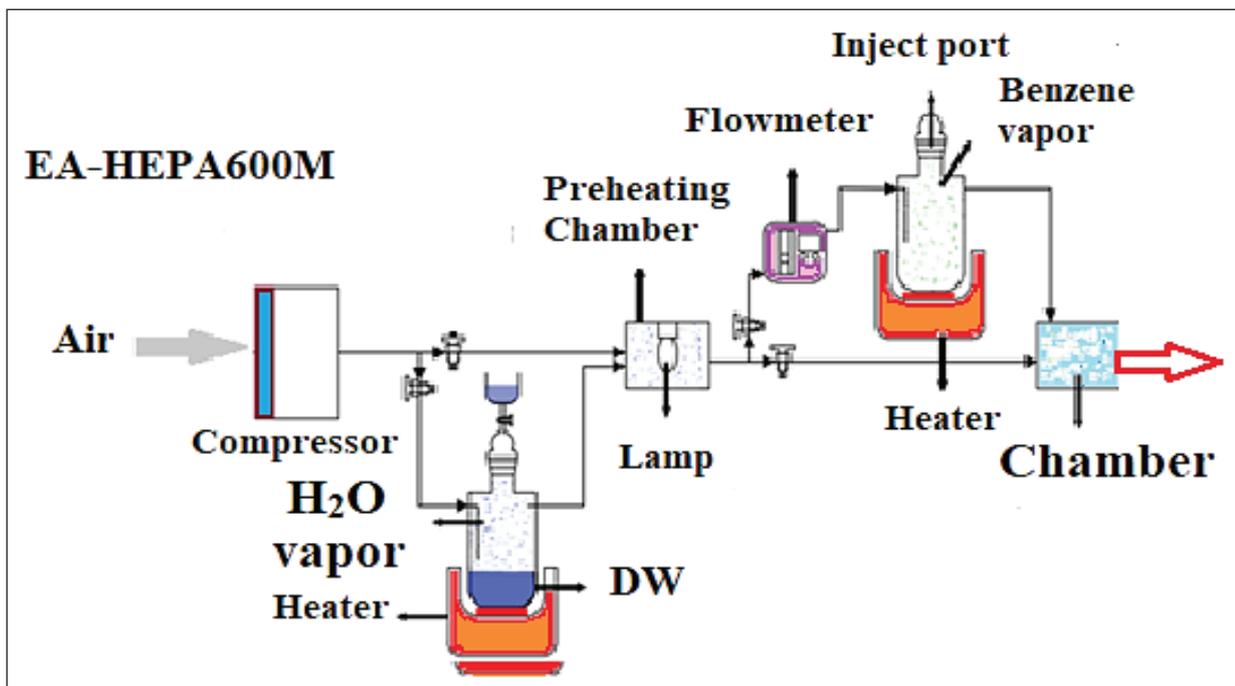


Fig.2. The generation of benzene vapor in pure air by chamber

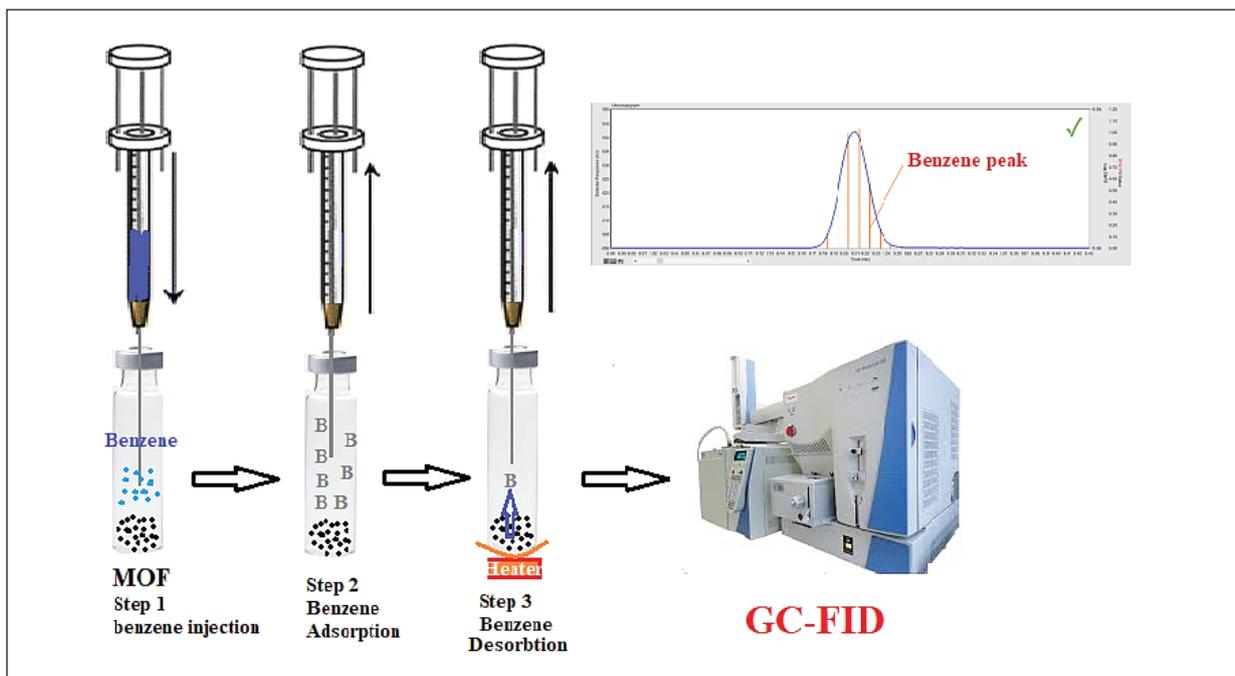


Fig.3. Static procedure for benzene removal from air by the Ta-MOF adsorbent

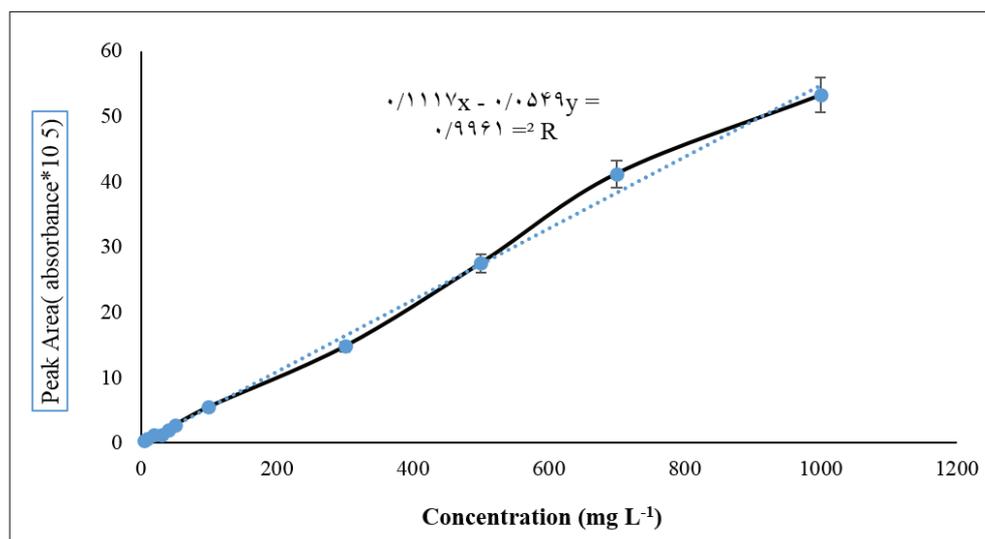


Fig.4. The calibration curve of benzene based on Ta-MOF adsorbent by GC-FID

The adsorption efficiency for static adsorption was obtained from the following equation:

$$Q = \frac{(C_0 - C_e) \times V}{m}$$

In the equation, Q is adsorption efficiency in (mg g^{-1}), C_0 is benzene's primary concentration in (mg L^{-1}), C_e is benzene's equilibrium concentration in the vial in (mg L^{-1}), m is the amount of adsorbent in (g), and V is the vial's volume in (L).

To draw the calibration curve from different standard concentrations of benzene in the ranges between 10 - 1000 mg L^{-1} were prepared in Tedlar sampling bags. Then, 100-500 microliters of the air vial containing benzene were prepared by a micro GC syringe. At last, the calibration curve was plotted by considering standard solutions and adsorption peak areas by GC-FID (Fig.4).

By dynamic procedure, 20 mg of Ta-MOF sorbent tubes connected to a sampling pump (SKC, UK). The flow rate was adjusted to 50-400 mL min^{-1} . The benzene vapour was mixed with pure air in the chamber, the different value of benzene in the air was passed through the Ta-MOF sorbent. After adsorption of benzene on Ta-MOF, the adsorbent was heated by thermal accessory at 80-100 $^{\circ}\text{C}$ in the presence of Ar gas and then, the benzene was

desorbed from Ta-MOF and flowed/stored in a polyethylene bag. Finally, the 100 -500 microliters of air were aspirated with Hamilton syringes and injected into an injector of GC-FID. Based on the dynamic procedure, Ta-MOF had efficient extraction and recovery for the removal of benzene from the air. The results showed that the absorption capacity of the static system was higher than the dynamic system at a flow rate of 250 ml min^{-1} .

3. Results and Discussion

3.1. SEM, TEM and XRD analysis

The morphology and size distribution of Ta-MOF nanoparticles were studied by a scanning electron microscope (SEM) and transmission electron microscopy (TEM). In this study, characterization of tantalum MOF adsorbent was carried out by SEM, TEM and XRD devices. SEM's microscopic images of Ta-MOF showed that the average size of particles in tantalum MOF adsorbent is 48 nanometers (Fig.5a). TEM of Ta-MOF showed a nanometric size of about 30 nm. The Ta-MOF sample has homogenous morphology with similar particle size (Fig.5b). Also, XRD images showed that tantalum MOF adsorbent has a cubic crystal structure (Fig.6). the X-ray diffraction pattern of porous Ta-MOF that prepared by the ultrasonic method. A comparison of Ta-MOF diffraction with the other MOF revealed a triclinic crystalline structure of Ta-

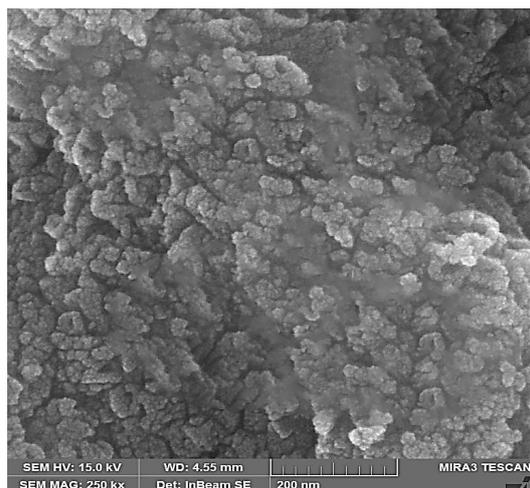


Fig. 5a. SEM images of tantalum Ta-MOF

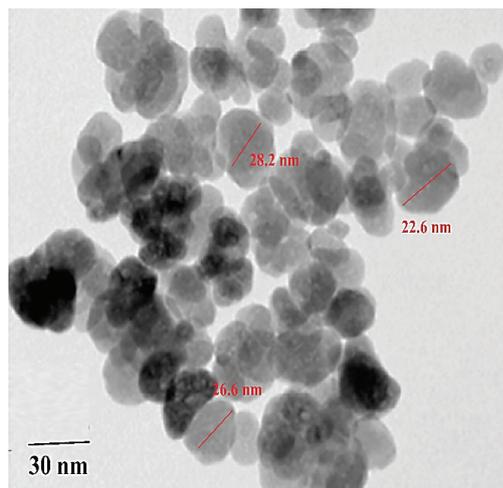


Fig. 5b. TEM images of tantalum Ta-MOF

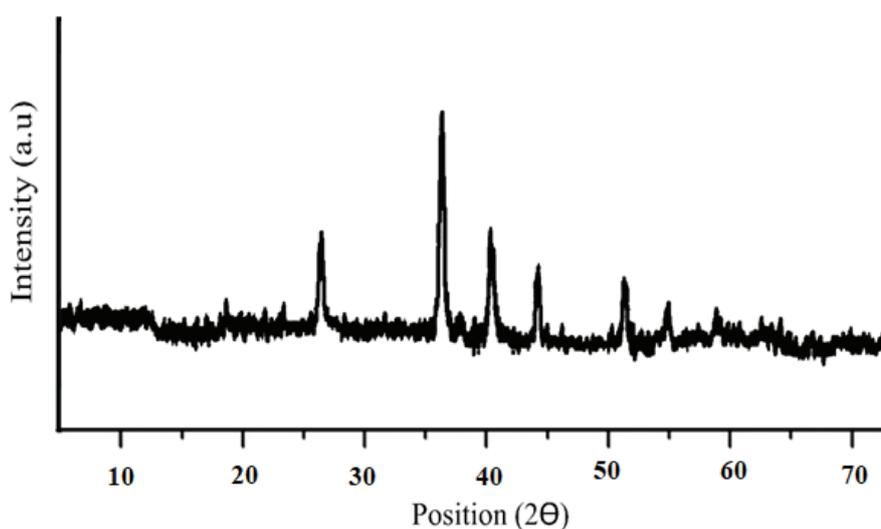


Fig. 6. XRD images of the tantalum MOF adsorbent

MOF. As TEM images any agglomeration wasn't seen in the structure of Ta-MOF.

3.2. The effect of benzene concentration on adsorption efficiency

The effect of benzene's primary concentration varying from 10 to 100 mg L⁻¹ on tantalum MOF adsorbent was studied. The results showed tantalum adsorbent became saturated at a concentration of 70 mg L⁻¹ (Fig. 7).

3.3. The Effect of exposure time on adsorbent efficiency

The effect of different times from 5 to 20 minutes

for benzene removal based on tantalum MOF in different concentrations of benzene between 10-100 mg L⁻¹ was studied. In this study, it was observed that increasing the exposure time has a positive effect on the recovery and adsorption capacity of Ta-MOF adsorbent. The results showed, the adsorption rate increases up to 10 minutes and then remains almost constant (Fig.8).

3.4. The effect of the amount of Ta-MOF on adsorption efficiency

The effect of the amount of the adsorbent (Ta-MOF) in the range of 0.1 to 2 mg for benzene removal include the benzene concentration (10 - 100 mg L⁻¹)

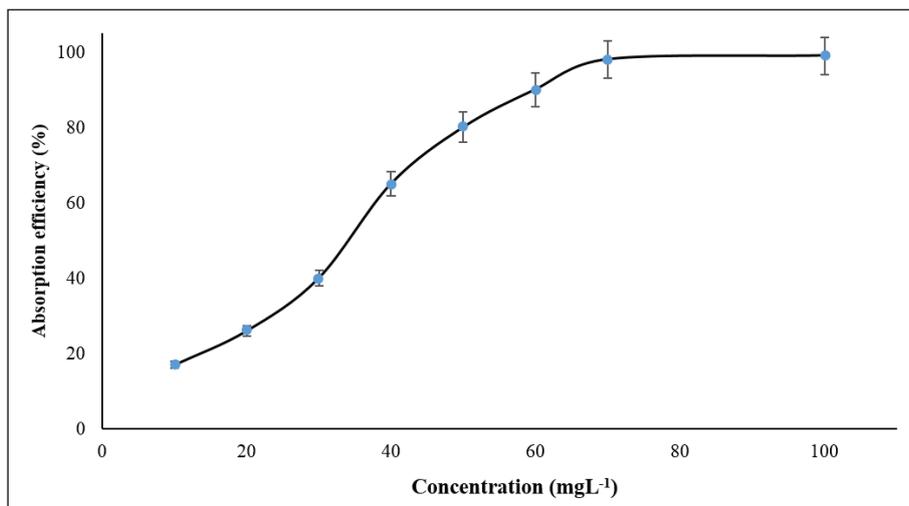


Fig.7. The effect of benzene concentration on Ta-MOF adsorption efficiency

was studied in optimized conditions. The results showed the maximum adsorption efficiency for benzene was achieved for 0.5 mg of Ta-MOF by 70 mg L⁻¹. Due to Figure 9, for an extra amount of adsorbent, the adsorption capacity increased and then constant (Fig. 9).

3.5. The effect of temperature on adsorption efficiency of Ta-MOF

For efficient removal of benzene from the air, the effect of temperature on adsorption/desorption of Ta-MOF must be optimized. The results showed us, the optimized temperature for adsorption and desorption of benzene from sorbent was achieved

at 45 °C and 90 °C, respectively. The effect of temperature on benzene removal was studied in optimized conditions. For this purpose, the different concentrations of benzene in the range of 10 to 100 mg L⁻¹ of benzene at a temperature between 25 - 60°C were evaluated. The results showed us, the maximum absorption capacity and efficiency were obtained at the temperature of 45 °C. For evaluating, 100-500 microliters of air containing benzene in static and dynamic procedure injected into GC. As shown in Figure 10, by increasing temperature, the absorption capacity and efficiency decreased (Fig.10).

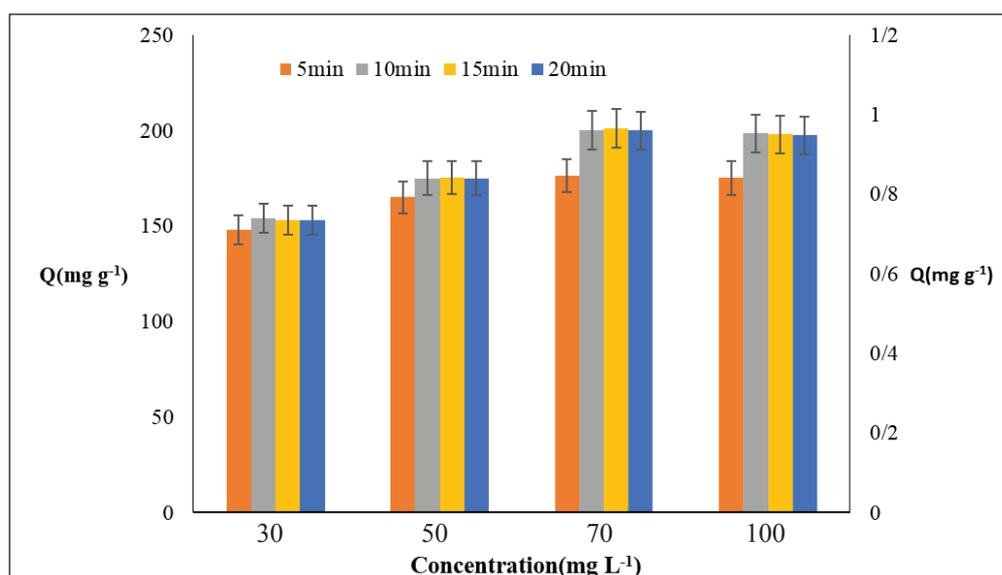


Fig. 8. The Effect of exposure time on adsorbent efficiency

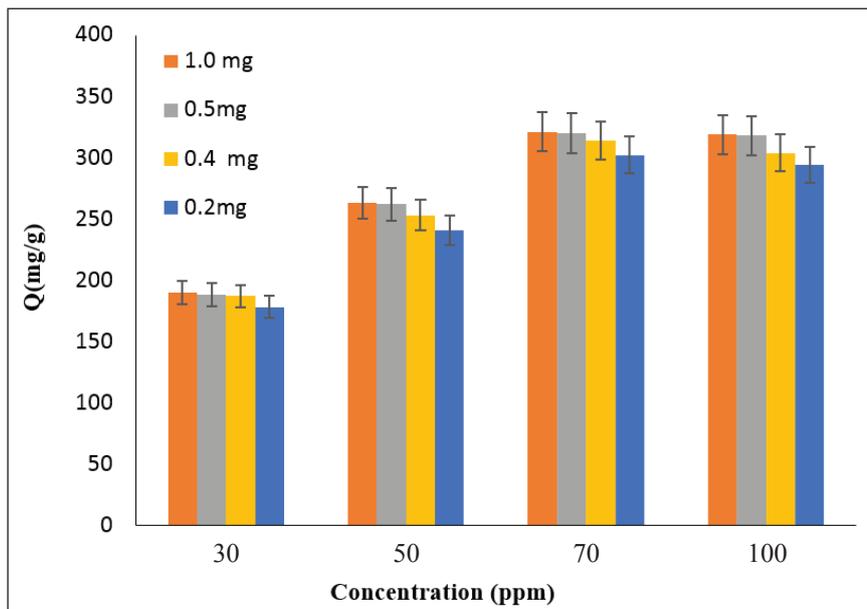


Fig. 9. The effect of the amount of Ta-MOF on adsorption capacity

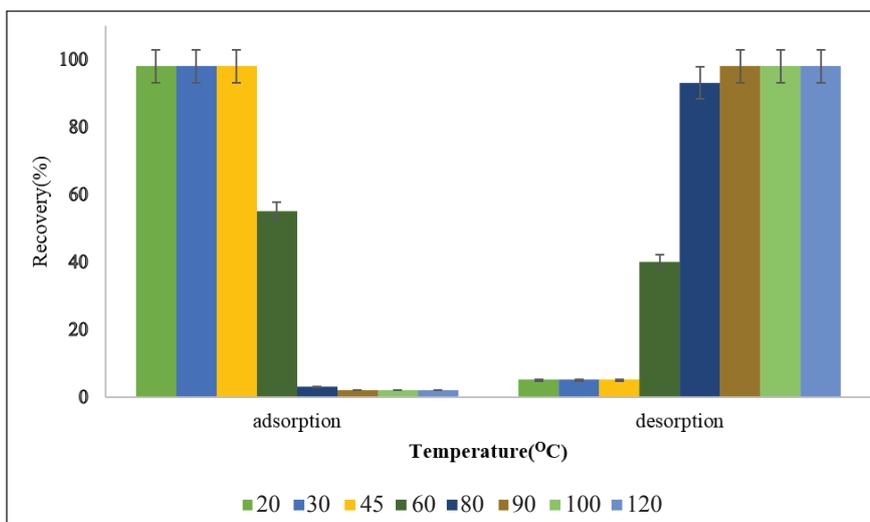
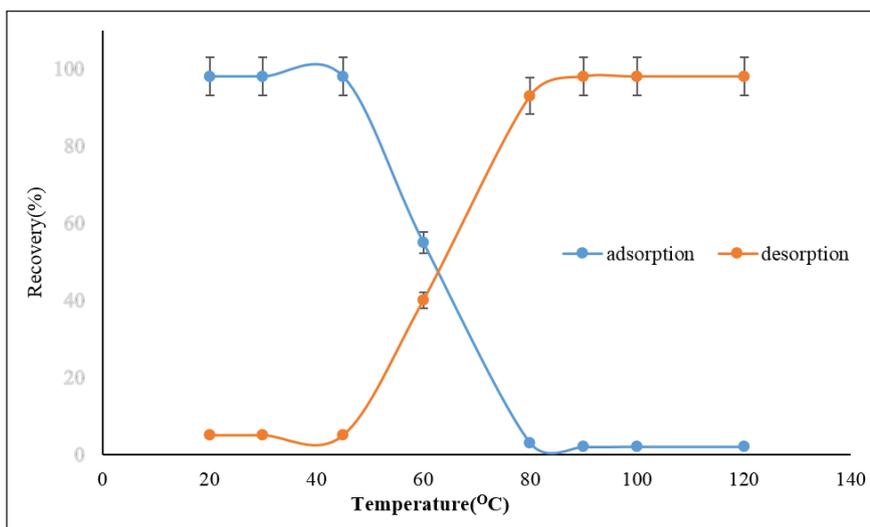


Fig.10. The effect of temperature on adsorption efficiency of Ta-MOF

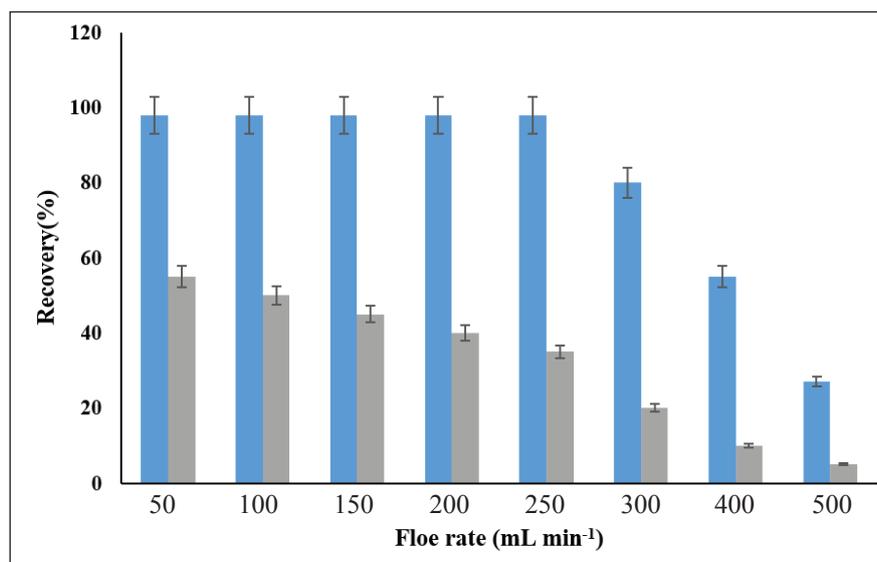


Fig.11. The effect of flow rate on adsorption efficiency of Ta-MOF (blue, 45 °C; grey, 60 °C)

3.6. Effect of flow rate

By procedure, the effect of different flow rates between 50 -500 mL min⁻¹ was studied by Ta-MOF adsorbent. The flow rate was measured by a digital rotameter. The removal efficiency and adsorption capacity of Ta-MOF were reduced in more than 300 mL min⁻¹ of flow rate. So, 250 mL min⁻¹ of flow rate was used as optimum flow rate for removal of benzene from the air. A higher

flow rate was significantly reduced the adsorption efficiency of benzene. Figure 11 shows the removal efficiency and adsorption capacity decreased by increasing the flow rate in optimized temperature (blue, 45 °C). Therefore, benzene cannot absorb at a higher flow rate by the sorbent. The results showed us the removal efficiency and the adsorption capacity was decreased at 60 °C (grey).

Table 1. Validation of GF-SPI method in a dynamic system based on Ta-MOF adsorbent by spiking benzene (ppm)

Air Samples	Added(ppm)	GF-SPI, GC-FID ppm	Recovery (%)
A	---	11.9 ± 0.4	---
	10	21.7 ± 1.1	98.1
B	---	18.5 ± 0.8	---
	20	38.2 ± 1.7	98.5
C	---	31.7 ± 1.4	---
	30	61.9 ± 2.9	100.6

^aMean of three determinations ± confidence interval (P = 0.95, n = 5)

3.7. Validation of methodology

The Ta-MOF was used for the removal of benzene vapour from the air. By the proposed method, a mixture of 10-100 ppm of benzene vapour in pure air (Ar gas) was passed through Ta-MOF sorbent by an SKC pump. Before adsorption, the standard of benzene in the air was validated by GC-MS in different concentrations. For validation, the spiked benzene concentration was done to demonstrate the reliability of the method by Ta-MOF (Table 1). At optimized conditions, at different times based on 250 mLmin⁻¹, the different concentrations of benzene in the air were generated and used for validation by spiking samples. The efficient recovery of spiked samples confirmed the capability of flow solid-phase interaction (GF-SPI) for the removal of benzene from the air.

3.8. Discussion

MOF adsorbent is one of the strongest adsorbents regarding the removal of volatile compounds from the air. In this study, the effect of tantalum organic metal framework adsorbent (Ta-MOF) for the removal of benzene vapour was investigated. The efficiency of different MOF adsorbents for benzene adsorption is shown in Table 2. Due to results, the tantalum MOF adsorbent has a higher adsorption efficiency as compared to the other adsorbents. In 2010, Lu and colleagues conducted a study regarding the removal of benzene, toluene, ethylbenzene, and para-xylene with carbon nanotubes oxidized by sodium hypochlorite and concluded that at first, with the increase of

exposure time, benzene adsorption efficiency also increased and then decreased [37]. As compared to the Ta-MOF, by increasing exposure time, the adsorption efficiency increased. Moreover, the maximum amount of adsorption occurred at 10 minutes and then the amount of adsorption remained constant. Also, in 2018, Hua Xie and colleagues carried out a study and concluded that the increase in temperature when using the MOF adsorbent, BUT-66 (Zr), lowered adsorption efficiency. In this study, it was found that the adsorbent at 25 and 80 °C had 2.54 mmol g⁻¹ and 1.65 mmol g⁻¹ of benzene adsorption, respectively [5], while in the present study at 25 and 45 °C, by increasing temperature, the amount of adsorption has decreased slightly. Also, the effect of temperature in the different adsorbents such as nano activated carbons and activated carbon has also been observed, which is confirmed by the study of Golbabai et al. to remove xylene vapor by these adsorbents. The results from Bright and colleagues research in 2008 regarding benzene adsorption efficiency using the adsorbents such as (MOF-5) (Zn₄O(CO₂)₆), (MOF-3)(C₈H₅NO₄-2), (MOF-177) (Zn₄O(btb)₂) and (MOF-199) (Cu₂(CO₂)₄), at benzene concentration levels of 440 ppm, showed that benzene adsorption efficiency for each 1gr adsorbent, was 2, 56, 1, and 176 milligrams of benzene, respectively [38]. However, in the present study, a trace amount of Ta-MOF can be absorbed by a high concentration of benzene (70 ppm) with a significant adsorption rate of 155.3 mg g⁻¹ which indicated the high adsorption capacity of the Ta-MOF adsorbent.

Table 2. Comparing of adsorption capacities of Ta-MOF with other adsorbents

Adsorbate	Adsorbents	A _{sur} (m ² g ⁻¹)	Q _a	T	Refs.
Benzene	(Zn ₄ O(CO ₂) ₆) MOF-5	2205	2 mg g ⁻¹	25° c	[24]
	(C ₈ H ₅ NO ₄ -2)IRMO-3	1568	56 mg g ⁻¹	25° c	[24]
	(Zn ² O ₂ (CO ₂) ₂)MOF-74	632	96 mg g ⁻¹	25 °c	[24]
	(Zn ₄ O(btb) ₂)MOF-177	3875	1 mg g ⁻¹	25 °c	[25]
	(Cu ₂ (CO ₂) ₄)MOF-199	1264	176 mg g ⁻¹	25 °c	[24,25]
	IRMO-62	1814	109 mg g ⁻¹	25 °c	[24]
	MIL-101 (Cr)	3980	1291±77 mg g ⁻¹	25 °c	[17]
	Ta-MOF	1200	350 mg g ⁻¹	45 °c	This study

4. Conclusion

In the present study, a new Ta-MOF adsorbent was used for the removal of benzene from air and the absorption efficiency studied. For benzene analysis, 100-500 microliter air from the vial (static) or polyethylene bag (dynamic) was extracted and injected into the GC-FID analyzer. To evaluate the adsorbent capacity, the effect of four independent factors such as benzene concentration, the adsorbent amount, the exposure time, and temperature on the amount of benzene adsorption were investigated. The absorption capacities of static and dynamic procedures based on Ta-MOF were obtained 155.3 mg g⁻¹ and 124.6 mg g⁻¹, respectively based on 0.5 g of Ta-MOF and the flow rate of 250 mL min⁻¹. The results showed the Ta-MOF adsorbent had more adsorption capacity than other conventional adsorbents.

5. Acknowledgements

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6. References

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