Vapour breakthrough behaviour of carbon tetrachloride - a simulant for chemical warfare agent on ASZMT carbon

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ASZMT (Cu, Ag, Zn, Mo, TEDA impregnated) carbon was prepared by impregnation of active carbon with ammonical salts of Cu (II), Ag (I), Zn (II), Mo (VI) and TEDA using incipient wetness technique. Thereafter, ASZMT carbon was characterized using scanning electron microscopy, atomic absorption spectroscopy, thermogravimetry and surface characterization techniques. The ASZMT carbon was evaluated under dynamic conditions against carbon tetrachloride vapour that was used as a simulant for the persistent chemical warfare agents for testing breakthrough times of filter cartridges and canisters of gas masks in the National Approval Test of Respirators. The effect of carbon tetrachloride concentration, test flow rate, temperature and relative humidity on the breakthrough behaviour of the ASZMT carbon for CCl_4 vapour has also been studied. The study clearly indicated that the ASZMT carbon provided adequate protection against carbon tetrachloride vapours. The breakthrough time decreased with the increase of the carbon tetrachloride concentration and flow rate. The variation in temperature and relative humidity did not significantly affect the breakthrough behaviour of ASZMT carbon at high vapour concentration of carbon tetrachloride whereas breakthrough time of ASZMT carbon reduced by an increase of relative humidity at low carbon tetrachloride vapour concentration.

Keywords: Active carbon, ASZMT carbon, Impregnation, Carbon tetra chloride vapour, Breakthrough time.

Introduction

Vapour breakthrough behaviour of carbon beds challenged with the air containing toxic chemicals is of great interest in connection with respiratory protection against hazardous chemicals[1,2]. Porous materials, having large surface area and pore volume, including zeolites[3], resins[4], activated carbon together with their derivatives[5], are the most frequently utilized adsorbents with high adsorption capacity for volatile organic compounds (VOCs). Metal–organic frameworks (MOFs), a new class of hybrid porous solids, are potentially a type of prominent porous adsorbents for VOCs because of the extremely large pore volume and surface area (usually >3000 m^2/g). In the last few years MOFs have been reported for the removal of carbon tetrachloride[6,7] and CW agents from air[8]. The major limitation with the use

of MOFs is its moisture sensitive nature which restricts it to be used in nuclear, biological and chemical (NBC) filtration systems.

Active carbon of high surface area has been widely used for the purification of the air and water owing to the adsorption capacity of this universal adsorbent[9]. Active carbon removes the wide range of chemicals based on physisorption, which depends upon its porous structure[10]. In order to increase the capacity of active carbon for adsorbate degradation it is pre-impregnated with chemicals[11], which add chemical degradation property to the physisorption capacity of carbon. Active carbon impregnated with salts of Cu(II), Cr(VI) and Ag(I) (Whetlerite carbon)[12] is presently used in NBC filtration systems for the removal of persistent CW agents such as blister and nerve agents and non-persistent chemical warfare (CW) agents such as hydrogen cyanide, phosgene and cyanogens chloride[13]. Various kinds of impregnated carbons those have reactivity towards CW agents have been prepared by Singh et al[14,15].

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Impregnated carbons such as $NaOH/CrO_3/C$, $NaOH/CrO_3/EDA/C$ and $RuCl_3/C$ has been used by Prasad et al to study its breakthrough behaviour for diethyl sulphide and sulphur mustard at low concentration[16,17].

Ideally the material used in NBC filtration systems should be of such type, which can provide filtered air against the whole spectrum of CW agents and do not get affected with the atmospheric moisture. The material also does not pose any problem of cross contamination, safe handling, carcinogenicity and disposal. Impregnated carbon is still the best material to be used in NBC filtration systems. NBC carbon at present used in air filtration systems contains Cr(VI) which is reported to be carcinogenic, having lesser shelf life and possess disposal problem. To overcome with all mentioned drawbacks ASZMT carbon (active carbon impregnated with salts of Cu (II), Ag (I), Zn (II), Mo (VI) and triethylene diammine (TEDA) was prepared and has been evaluated against carbon tetrachloride (CCl_4) vapours[18] to asses this for their protection capacity against CW agents such as blister agents and nerve agents of high boiling points. CCl_4 vapour has long been used as a simulant for the CW agents for testing breakthrough times of gas mask cartridges and canisters in the National Approval Test of Respirators[2,19,20]. Preliminary study with the use of simulants of CW agents is always recommended prior to use against actual agents, it is because of their less toxicity, structure resemblance and closer molecular dimensions to that of actual agents[21,22].

Similarity of vapour pressure, water-insolubility and technical feasibility in generating a test airflow containing the vapour ranging from low to high concentration, and the lower risk in toxicity are the primary requirement to single out a CW replacement vapor. Testing of ASZMT carbon (to be used against CW agents) with simulant such as CCl_4 vapours has several advantages for example the test agent has lower toxicity, requires fewer handling precautions and fewer special facilities, and no licensing for field use. It also allows more frequent tests due to lower cost of the test agent. There is no CW contamination of the test bed and no release of CW vapour in the bed effluent[23]. Various simulation methods were also been used to calculate the adsorption potential of carbon for CCl_4[24,25].

Materials and Methods
Materials
Active carbon coconut shell origin, 90 CTC grade of 12 x 30 BSS (1.40-0.50 mm) particle size and surface area about 1359 m^2/g was procured from M/s Active carbon India, Pvt. Ltd, Hyderabad, India. $CuCO_3.Cu(OH)_2$, $AgNO_3$, $ZnCO_3.2ZnO.3H_2O$, $NH_4Mo_6O_{24}.7H_2O$, $C_6H_{12}N$ and CCl_4 (AR grade), were obtained from M/s SD fine chemicals. Mini RAE 3000 VOC monitor from M/s RAE Systems, USA was used for the detection of CCl_4 vapour and KDS dual-syringe pump series 200 was procured from Sigma-Aldrich, India.

Preparation of ASZMT Carbon
ASZMT carbon was prepared by impregnation of active carbon with Cu (II), Ag (I), Zn (II), Mo (VI) and TEDA using incipient wetness technique. $CuCO_3.Cu(OH)_2$, $AgNO_3$, $ZnCO_3.2ZnO.3H_2O$, $NH_4Mo_6O_{24}.7H_2O$ and $C_6H_{12}N$ was used as precursors. Cu (II), Ag (I), Zn (II) was impregnated in first stage and Mo (VI) and TEDA was impregnated in the second stage.

Characterization of ASZMT Carbon
The morphology and microstructure of the ASZMT carbon was characterized by surface area analyzer, scanning electron microscope (SEM) and thermo gravimetric (TGA) analyzer. The metal ion contents were determined by atomic absorption spectrophotometer (AAS). Surface area, micro pore volume, cumulative pore volume and pore size distribution were measured by nitrogen adsorption at 77 K using Autosorb 1C from Quantachrome Instruments, USA. The surface area was calculated from the Brunauer-Emmett-Teller (BET) method. Micropore volume from the Dubinin-Radushkevich equation (DR) method whereas, cumulative desorption pore volume were calculated from the Barrett, Joyner and Halenda (BJH) equation. Pore maxima for mesopores and micropores were obtained from BJH method. The metal ions loading were determined by extracting metal ions from ASZMT carbon in acidic medium. Cu (II), Ag (I), Zn (II), Mo (VI) were extracted using 10% HNO_3 and thereafter estimating by AAS, GBC Avanta PM, Australia. For scanning electron microscopic characterization, the powder samples were first mounted on brass stubs using double sided adhesive tape and then gold coated for 8 minutes using ion sputter JEOL, JFC 1100 coating unit. The surface texture of the catalyst was observed using FEI ESEM Quanta 400. Thermo gravimetric analysis of catalyst was performed on a thermogravimetric analyzer, TGA-2920 from TA Instruments, USA. Thermograms for materials were recorded from 40 to 700 °C at a heating
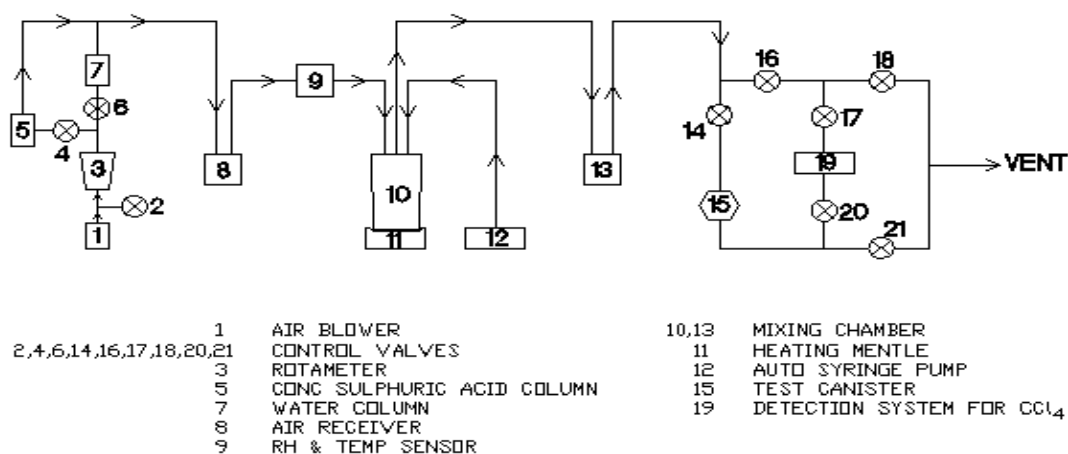
1	AIR BLOWER	10,13 MIXING CHAMBER
2,4,6,14,16,17,18,20,21 CONTROL VALVES		11 HEATING MENTLE
3	ROTAMETER	12 AUTO SYRINGE PUMP
5	CONC SULPHURIC ACID COLUMN	15 TEST CANISTER
7	WATER COLUMN	19 DETECTION SYSTEM FOR CCl₄
8	AIR RECEIVER	
9	RH & TEMP SENSOR	

Figure 1——Test rig for CCl$_4$ vapour adsorption studies of ASZMT carbon.

Table 1——Surface area and micro pore volume details of the active and ASZMT carbon

Carbon systems (m^2/g)	Surface area (N$_2$ BET)	Micro pore volume (N$_2$ DR) (cm^3/g)	BJH Cumulative desorption pore volume (N$_2$BJH) (cm^3/g)	Pore maxima (Å)	
				(micropore)	(mesopore)
Active carbon	1359	0.70	0.33	9.26	23.29
ASZMT carbon	963	0.50	0.25	13.97	21.40

rate of 10 °C min^{-1} under nitrogen atmosphere. Bulk density, moisture content and hardness were measured using ASTM test method D 2854-96, D 2867-95 and D 3802-79 respectively.

CCl$_4$ Breakthrough Measurements of ASZMT Carbon

CCl$_4$ breakthrough measurements of ASZMT carbon were carried out in the glass column under continuous flow at atmospheric pressure. A detailed description and schematic representation of the experimental set-up for CCl$_4$ breakthrough measurements of ASZMT carbon is shown in Fig. 1. As depicted in Fig. 1 the air was taken from air blower (1) in the mixing chamber (8) at required flow rate through rotameter (3) using a control valve (2). Proper relative humidity (RH) was generated in the air before sending to mixing chamber by passing it in the required ratio through concentrated sulphuric acid chamber (5) and water chamber (7) using a control valve (4) and (6). The RH of the mixed air was monitored using the RH meter (9). Air of known RH was mixed with CCl$_4$ vapours, injected from auto syringe pump (12), in the mixing chamber (10). Injected CCl$_4$ was converted to its vapours by heating with heating mantle (11). To mix CCl$_4$ vapours properly with air, this mixture of air and CCl$_4$ vapours was sent to another mixing chamber

(13). CCl$_4$-air mixture thus generated was tested for the presence of CCl$_4$ with the detection system (19) using control valves (14, 16, 17 and 18). Test carbon (15) was evaluated for CCl$_4$ vapour breakthrough time (btt) by sending the CCl$_4$-air mixture through it using the control valves (14 and 16). CCl$_4$ vapour breakthrough time and breakthrough concentration (1 ppm) was monitored at the outlet of the glass column with the VOC monitor (19) equipped with an automatic gas sampling device and a photo ionization detector (PID) of 11.7 eV using the control valves (20 and 21).

Results and Discussion

Textural Properties

Active carbon of 1359 m^2/g surface area when was impregnated with impregnants showed the decrease in surface area (Table 1) from 1359 to 963 m^2/g. This may be due to the impregnants, which probably occupies some of the micro pore openings and also gets deposited in meso pores and bring down the surface area. The N$_2$ DR micropore volume and N$_2$ BJH cumulative desorption pore volume also indicated the decrease in values with ASZMT carbon, as active carbon showed higher value (0.70 and 0.33 cm^3/g) than ASZMT carbon (0.50 and 0.25 cm^3/g) respectively (Table 1).
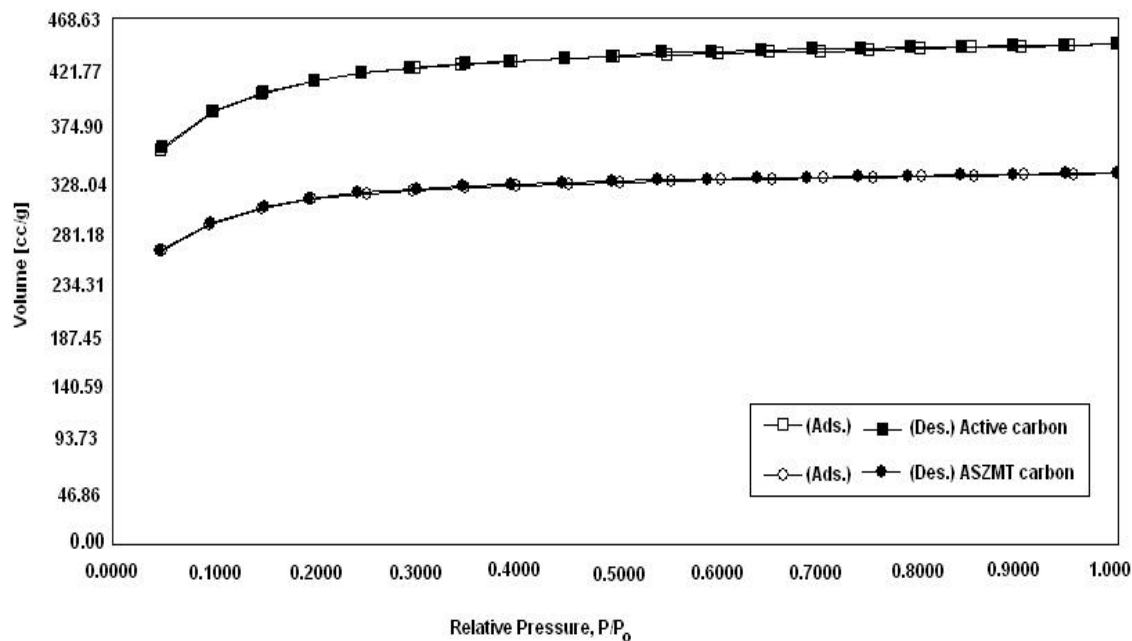
Figure 2——N$_2$ adsorption desorption isotherms of active and ASZMT carbon in N$_2$ at 77 K.

Table 2——Metal ion contents in active and ASZMT carbon

Element(%)	Active carbon	ASZMT carbon
Cu	Nil	6.0
Ag	Nil	0.2
Zn	Nil	6.0
Mo	Nil	2.5
TEDA	Nil	3.5

Table 3——Test condition for the evaluation of the ASZMT carbon

Parameter	Specified value
Bed height of ASZMT carbon	25.0 (20.5-27.0) mm
Column diameter of column	20.0 mm
Test flow rate	1.25 (0.8-1.5)lpm
CCl$_4$ inlet concentration	53.13 (5.314- 212.52) mg/L
Breakthrough CCl$_4$conc.	1 ppm
Temperature	25 ±2 (20-60) °C
Relative humidity (RH)	75 ±5 (0.2-80)%

Note: Values in the bracket shows the variation in the parameters.

Fig. 2 shows the adsorption desorption isotherms of active and ASZMT carbon respectively, which indicate the adsorbents to be micro porous. The only difference between the different materials upon nitrogen adsorption is the value of the saturation plateau obtained at high relative pressures, which indicates different micropore and mesopore volumesAu:[26]. The isotherms of active carbon and ASZMT carbon remained unchanged, which means the microporus structure of the carbon is retained even after impregnation. BJH pore size distributions indicates mesopore maxima at 23.29 and 21.40 Å and micropore maxima at 9.36 and 13.27 Å respectively. Active carbon and ASZMT carbon have bulk densities to be 0.32 and 0.60 g/mL respectively. Bulk density of ASZMT carbon was found to be higher than the active carbon because pores in ASZMT carbon were occupied by metal salts. Moisture content of active carbon and ASZMT carbon was found to be 5.0 and 1.2 % respectively. Hardness of the active carbon and ASZMT carbon was found to be 97 and 96 % respectively.

Table 2 indicates the concentration of metal ions extracted from the ASZMT carbon. It indicates that the extracted metal contents (experimentally calculated) are within the close agreement of impregnation percentages (theoretical values).

Table 3 indicates the test conditions for the evaluation of ASZMT carbon. ASZMT carbon was evaluated at CCl$_4$ concentration 53.13 mg/L, test flow rate 1.25 lpm, bed height 25.0 mm, temperature 25 ± 2°C and RH 75 ± 5%. ASZMT carbon was also evaluated at different CCl$_4$ concentration varying from 5.314- 212.52 mg/L, test flow rate from 0.8-1.5 lpm, temperature from 20-60°C and RH from 0.2 to 80%.

The SEM images of active carbon and ASZMT carbon are shown in [Fig. 3 (a & b)]. A SEM image of
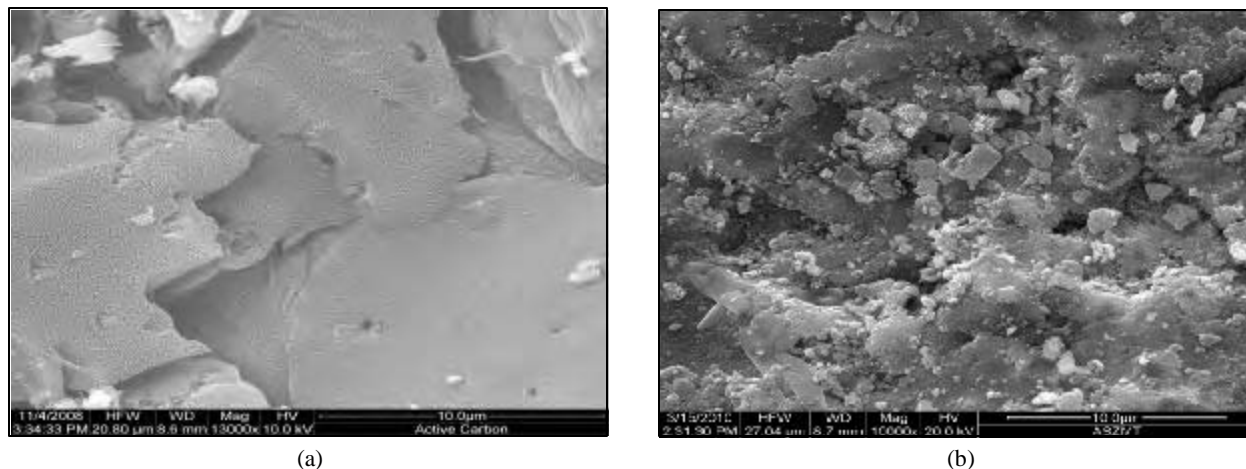
(a)

(b)

Figure 3——SEM images of (a) active carbon (b) ASZMT carbon.
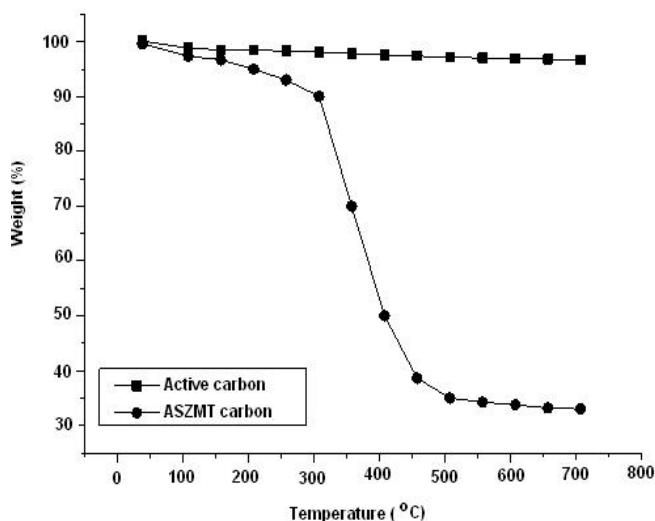

Figure 4——TGA curves of active and ASZMT carbon.

active carbon showed considerable small cavities, cracks and attached fine particles over the surface, forming a system of complicated pore networks [Fig. 3 (a)]. After impregnation with metal salts leads to the clogging of the cracks and cavities by the adsorbed metal salts, and dispersal of metal salts on the surface of ASZMT carbon [Fig. 3 (b)]. A SEM image of ASZMT carbon clearly showed the metal salts particles as white spots.

Fig. 4 illustrates weight change as a function of temperature for active carbon and ASZMT carbon in nitrogen atmosphere. The weight loss data as a function of increasing temperature were collected and used to assess the effect(s) of the metal impregnants on the deterioration of the impregnated carbon. Adsorbed moisture starts getting removed at 110 °C. Fig. 4 showed the weight loss of about 1.5 and 3.0 % in active carbon

and ASZMT carbon at 110 °C because of the loss of adsorbed water molecules (moisture). ASZMT carbon exhibited about 10 % of weight loss up to 307 °C due to the oxidation of the carbon matrix by TEDA[27]. About 40 % weight loss took place between 307-407 °C. This sudden weight loss is due to the oxidation of the carbon by the impregnant species and subsequently the reduction of copper (II) oxide to copper (I) oxide. Thermal decomposition of the complexes of TEDA with metal salts deposited on carbon also took place at the temperature higher than 300 °C[27]. This hypothesis is supported by the behaviour of the active carbon where there are no impregnants available to oxidize the carbon. Ehrburger et al.[28] have reported similar results for chromium impregnated carbon. At temperature greater than 450 °C, a steady weight loss was observed up to a high temperature of 700 °C.

Stability and Reproducibility of Concentrations of CCl₄ Vapours in the Test Airflow

Stability of the CCl_4 vapour concentration in the test airflow was monitored as the variation coefficient (CV). Passing the air sample during 2 or 3 hours of constant running of the test airflow generating test rig, the CV of the vapour concentration was found to be 1.0% for time averaged concentration of 5.313 mg/L CCl_4 vapour in the test air flow. The CVs of CCl_4 vapor at different concentrations were also found to be within the same range from 1 to 1.2%. As to reproducibility in generating the test airflow, day-to-day variations of CCl_4 concentrations in the airflow were found to be within the range from 1 to 1.5%. High reproducibility of the CCl_4 vapour concentration in the test airflow was also
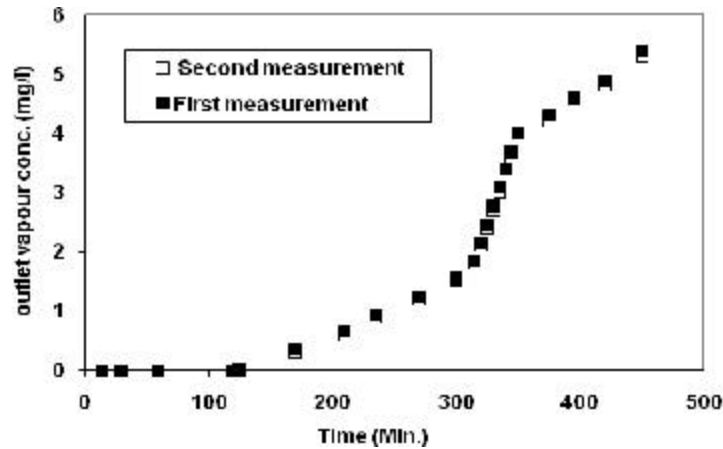
Figure 5——Vapour concentration of CCl_4 at the outlet of ASZMT carbon at 5.313 mg/L CCl_4 vapour inlet concentration.
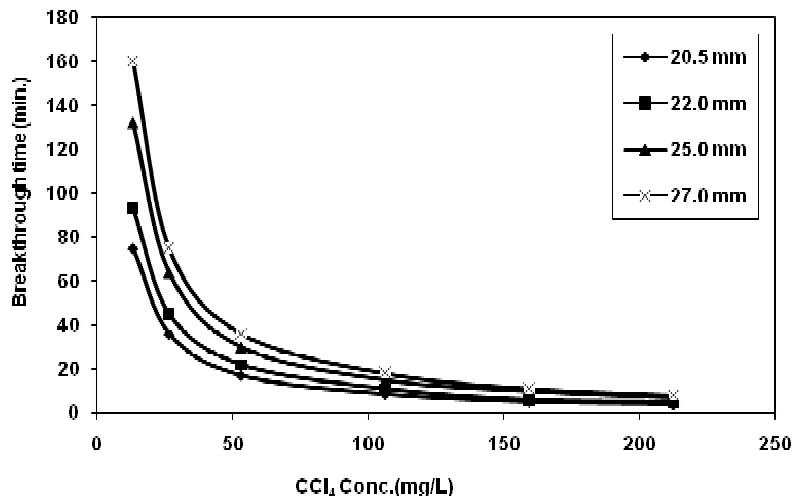

Figure 6——Effect of CCl_4 vapour concentration on the breakthrough behaviour of CCl_4 vapour for ASZMT carbon.

indicated by the breakthrough curves obtained by duplicated measurements in Fig. 5 which agreed well with each other. This means that the apparatus generated a stable and reproducible test airflow containing an organic vapour at a satisfactorily constant concentration.

Breakthrough Behaviour of ASZMT Carbon for CCl_4

Fig. 5 shows breakthrough curve of CCl_4 as a function of time elapsed from the start of passing the test airflow through the ASZMT carbon having bed height of 25.0 mm, test flow of 1.25 lpm and the inlet concentration of 5.313 mg/L (Table 3). The breakthrough concentration-time relationships were found to follow sigmoidal curves, indicating three distinct stages in the breakthrough concentrations: The first stage is

characterized by the beginning of the test vapour leakage into the exit airflow whose concentration increases slowly. In the practical uses of gasmasks, cartridges or canisters should be replaced with a new one at this stage before the exit vapour concentration reaches to the noxious level to the users. After this first stage, the exit vapour concentration rapidly rises and then reached to a plateau level approximated to the inlet concentration. The breakthrough times of the cartridges or canisters are defined as those when the vapour begins to leak from the test piece at the maximum permissible concentrations for the wearers on principle, but conventionally at 1 ppm in this study.

Effect of Bed Height and CCl_4 Concentration

Fig. 6 shows the relationship of breakthrough time of ASZMT carbon versus CCl_4 vapour concentration at
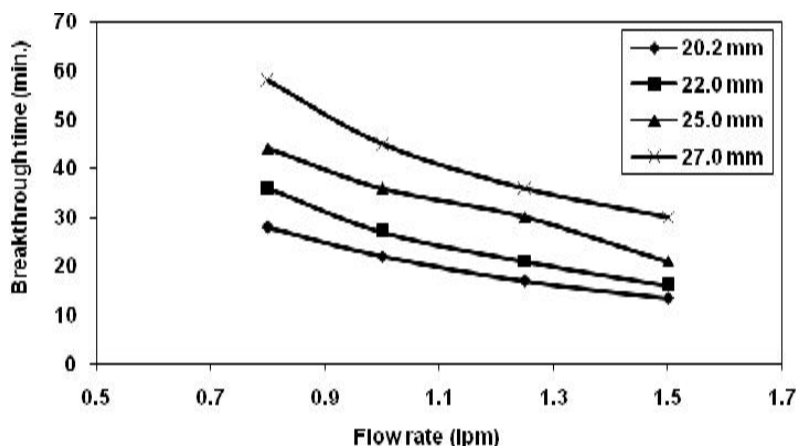
Figure 7——Effect of test flow rate on the breakthrough behaviour of CCl_4 vapour for ASZMT carbon.

varying bed height of carbon (20.5-27.0 mm) and inlet concentration (53.13- 212.52) mg/L, test flow of 1.25 lpm, (Table 3). Fig. 6 clearly indicates that the breakthrough time of ASZMT carbon decreases with the increase of the vapour concentration of CCl_4[29,30]. At the inlet concentration of 13.28 mg/L, the btt was found to be 75, 93, 132 and 160 minutes at the bed height of 20.5, 22.0, 25.0 and 27.0 mm respectively and at a CCl_4 vapour inlet concentration of 26.56, 53.13, 106.26, 159.39 and 212.52 mg/L the btt was observed to be decreasing to 36, 17, 8.5, 5.0 and 4.0 minutes respectively at the bed height of 20.5 mm whereas the btt values for ASZMT carbon was observed to be 75, 36, 18, 11 and 8.0 minutes respectively at the bed height of 27.0 mm. Results indicates that the btt of ASZMT carbon was found to be increasing with the increase of the bed height of carbon and decrease in the concentration of CCl_4.

Effect of Test Flow Rate and Temperature

Fig. 7 describes the effect of test flow rate on the CCl_4 vapour breakthrough behaviour of ASZMT carbon with different bed height (20.5-27.0 mm) and test flow (0.8-1.5) lpm at 53.13 mg/L inlet concentration (Table 3). At the inlet flow rate of 0.8 lpm, ASZMT carbon having bed height of 20.5, 22.0, 25.0 and 27.0 mm showed breakthrough time of 28, 36, 44 and 58 minutes respectively, while increasing the inlet flow to 1.25 lpm, the breakthrough time decreased to 17, 21, 30 and 36 minutes respectively and further increase of inlet flow to 1.5 lpm resulted into early CCl_4 vapour breakthrough and breakthrough time decreased to 13.5, 16, 21 and 30 minutes respectively. The trend of the change in the outlet CCl_4 vapour concentration with flow rate is as what one expects. With the increase of flow rate, the breakthrough

time decreases due to less contact time[2]. The contact time decreases from 0.56 to 0.32 sec when flow rate increases from 0.8 to 1.5 lpm.

Temperature variation in the range of 20-60 °C does not affect much the breakthrough behaviour of ASZMT carbon. In the temperature range of 20-40 °C, the btt of 17, 22, 30 and 36 minutes was observed at the bed height of 20.5, 22.0, 25.0 and 27.0 mm respectively, whereas the increase of temperature from 40 to 60 °C resulted into decrease of breakthrough time to 16, 21, 29 and 35 minutes respectively. This may be attributed due to fast desorption of CCl_4 vapour at higher temperature [2].

Effect of Relative Humidity

The performance of ASZMT carbon against CCl_4 - air mixture having different RH (0.2 to 80 %) at the inlet flow of 1.25 lpm and concentration of 53.13 mg/L indicates that ASZMT carbon does not show much variation in the breakthrough behaviour of CCl_4 vapour due to less susceptibility of ASZMT carbon with the coexisting moisture. This can be attributed to the fact that higher concentration of CCl_4 vapour causes more exothermic reaction which results into increase of the temperature of the adsorbent. This sudden increase of temperature nullifies the effect of high humidity. Result indicates that when the RH was increased from 0.2 to 80 % the breakthrough time of ASZMT carbon decreased from 17 to 16 minutes, 22 to 21 minutes, 30 to 29 minutes and 36 to 35 minutes at the bed height of 20.5, 22.0, 25.0 and 27.0 mm respectively.

Fig. 8 shows the effect of humidity on the breakthrough behaviour of CCl_4 vapours at the inlet flow of 1.25 lpm and concentration of 5.313 mg/L. Fig. 8 indicates that the breakthrough time of ASZMT carbon
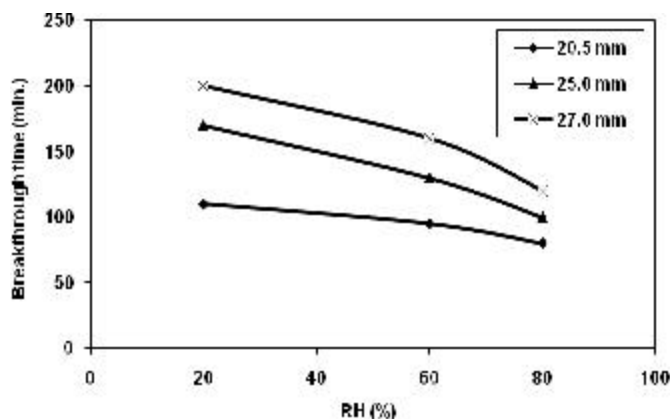
Figure 8——Effect of RH on the breakthrough behaviour of CCl_4 vapour for ASZMT carbon at the inlet concentration of 5.313 mg/L.

was shortened remarkably by an increase of RH from 20 to 80% in the airflow. An increase of RH from 20 to 80 % results into decrease of breakthrough time from 110 to 80 minutes, 170 to 100 minutes and 200 to 120 minutes at the bed height of 20.5, 25.0 and 27.0 mm respectively. Fig. 8 reveal clearly that the breakthrough times of ASZMT carbon for the test vapour in the lower concentration range are shortened significantly by the high humidity. This apparent difference in the breakthrough behaviour of ASZMT carbon for CCl_4 vapour at high humidity can be interpreted that CCl_4 and H_2O molecules adsorb competitively on carbon which in turn results into blockage of active sites of the carbon by H_2O adsorption[31, 32].

Conclusions

ASZMT carbon was prepared by impregnation of active carbon with ammoniacal salts of Cu (II), Ag (I), Zn (II), Mo (VI) and TEDA using incipient wetness technique. The prepared system was evaluated against CCl_4 vapour which was taken as a simulant for the CW agents to find out its protective potential against chemical warfare agents. The breakthrough behaviour of ASZMT carbon for CCl_4 vapours was studied. Effects of various parameters such as CCl_4 concentration, bed height, test flow rate, temperature and RH were studied and interpreted in terms of their CCl_4 btt values. CCl_4 btt values were observed to be decreasing with the increase in CCl_4 concentration and inlet flow rate and decrease in bed height of carbon. The variation in temperature and RH did not affect much the CCl_4 breakthrough behaviour of ASZMT carbon at high vapour concentration of CCl_4 whereas breakthrough times of ASZMT carbon were

shortened by an increase of RH at low CCl_4 vapour concentration. Therefore, it can be concluded that the ASZMT carbon can be used in air cleaning filters and canisters to provide protection against deadly toxic CW agents.

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