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Development and Evaluation of Impregnated Carbon Systems Against Iodine Vapours

Avanish Kumar Srivastava, Amit Saxena, Beer Singh♠ and Suresh Kumar Srivas

Defence Research and Development Establishment, Jhansi road, Gwalior-474002 (MP), India
♠e-mail: *beerbs5@rediffmail.com*

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Abstract

In order to understand the breakthrough behaviour of iodine vapours on impregnated carbon systems, an active carbon, 80 CTC grade, 12×30 BSS particle size and 1104 m^2/g surface area, was impregnated with metal salts such Cu, Cr, Ag, Mo and Zn, and an organic compound Triethylene diamine (TEDA) to prepare different carbon systems such as whetlerite, whetlerite/TEDA, whetlerite/KI/KOH and ASZMT. The prepared adsorbents along with active carbon were characterized for surface area and pore volume by N_2 adsorption at liquid nitrogen temperature. These carbon systems were compared for their CT (concentration X time) values at 12.73 to 53.05 cm/sec space velocities and 2 to 5 cm carbon column bed heights. The carbon column of 5.0 cm bed height and 1.0 cm diameter was found to be providing protection against iodine vapours up to 5.5 h at 3.712 mg/L iodine vapour concentration and 12.73 cm/sec space velocity. The study clearly indicated the adsorption capacities of carbon systems to be directly proportional to their surface area values. Dead layer with all the prepared carbon systems was found to be less than 2.0 cm indicating it to be minimum bed height to have protection against I_2 vapours. Effect of carbon bed height and flow rate was also studied. The active carbon showed maximum protection at all bed heights and flow rates in comparison to all other impregnated carbon systems, showing that only physical adsorption is responsible for the removal of iodine vapours.

Keywords : *Activated carbon, impregnated carbons, impregnation and iodine vapour*

1. Introduction

Active carbon of high surface area has been widely used for the purification of the air and water using the adsorption capacity of this universal adsorbent [1-3]. Active carbon removes the wide range of chemicals based on physisorption, which depends upon its porous structure. Porous structure of active carbon is mainly due to various pores such as macro, meso and micro contained within the adsorbent. Micro pores are mainly responsible for the adsorptive removal of chemical vapours of organic nature. In order to increase the capacity of active carbon by adsorbate degradation it is pre-impregnated with chemicals [4], which add chemical degradation property to the physisorption capacity of carbon. Silica gel, zeolites [5] and aluminum oxide are the other sorptive materials which are used for the removal of iodine vapours, but active carbon exhibits relatively better adsorptive properties than the other adsorbents and make them indispensable for use in respiratory cartridges [1-3].

ASC (copper, silver, chromium) Whetlerite [2] developed during World War II is a carbon, impregnated with metal salts of Cu (II), Cr (VI) and Ag (I). This impregnated carbon is being used in NBC(nuclear, biological and chemical) filtration system for the removal of persistent and non-persistent chemical warfare (CW) agents. It is understood that persistent CW agents such as blister and nerve agents are mainly held over the adsorbent surface due to physical adsorption, while nonpersistant gases such as hydrogen cyanide, cyanogen chloride and phosgene are converted into non-toxic products due to the chemical reaction with impregnated metal salts [2, 6-8]. Ideally the filtration systems should be of such type, which can provide filtered air against the whole spectrum of chemical warfare agents and do not pose any problem of cross contamination, safe handling and disposal. Therefore, there exists a need to develop adsorbent material for the filtration systems capable of degrading all type of CW agents chemically into non-toxic products. Vapour breakthrough behavior of carbon beds challenged with contaminated air streams is also of great interest in connection with respiratory protection against hazardous vapours.

Ideally the impregnated carbon used in NBC filtration systems should completely remove chemical and biological contamination along with the nuclear one. The removal of third type, i.e.; radio active elements and radio active elements tagged molecules such as radioactive ^{131}I tagged elemental I_2, organic iodine (CH_3I), etc. [9] can be achieved using activated carbon impregnated with KI/KOH. This carbon system removes radioiodine by isotope exchange [10].

Table 1. Surface Area and Micro Pore Volume Details of Prepared Carbon Systems

S. No.	Carbon systems	Surface area (N_2 BET) (m^2/g)	Micro pore volume (N_2 DR) (cm^3/g)	BJH Cumulative desorption pore volume (N_2 BJH) (cm^3/g)
1	Wh	1036	0.51	0.43
2	Wh/ TEDA	828	0.41	0.33
3	Wh /KI / KOH	900	0.45	0.37
4	ASZMT	684	0.34	0.28
5	Active carbon	1104	0.55	0.34

$$\underset{\text{(on adsorbent)}}{CH_3\,{}^{131}I} + K\,{}^{127}I \rightarrow \underset{\text{(on adsorbent)}}{CH_3\,{}^{127}I} + K\,{}^{131}I \qquad (1)$$

Activated carbon impregnated with amine compounds are also used to remove radio iodine by complex formation [10-19].

$$CH_3\,I + N(CH_2\,CH_2)_3N \rightarrow N(CH_2\,CH_2)_3NCH_3 + I^- \qquad (2)$$

Testing of adsorbents and adsorbers (to be used against radio iodine) with non-radiometric vapours has several advantages such as a lower toxicity, fewer handling precautions, 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 radioactive contamination of the test bed and no release of radioactive vapour in the bed effluent. Every compound has its distinctive adsorption or reactive behavior with a given adsorbent, therefore, the most useful tests of removal efficiency involve the same vapour to be trapped. Elemental iodine has also been used for laboratory measurements of adsorbent efficiencies and retentions [13]. This reduces the frequency of the costly and difficult procedures of taking representative samples and laboratory testing with radioiodines.

2. Experimental

2.1. Materials/Chemicals :

Active carbon coconut shell origin, 80 CTC (carbon tetra chloride) grade and surface area about 1104 m^2/g was procured from M/s Active carbon India, Ltd, Hyderabad, India. Iodine (AR grade), sodium thiosulphate and starch were obtained from M/s Sisco, M/s Ranchem and M/s SD fine chemicals Ltd respectively.

2.2. Carbon Systems

Following carbon systems with different percentage of impregnants (Table 2) were prepared by incipient wetness technique and evaluated against iodine vapours at various bed heights and flow rates to check the protective potential against iodine vapours:-

1 Active carbon: Active carbon of coconut shell origin and 80 CTC grade.

2 Whetlerite carbon: Activated carbon impregnated with ammonical solution of basic cupric carbonate, silver nitrate, chromium trioxide, pyridine and sodium hydroxide.

3 Wh/KI/KOH impregnated carbon: Whetlerite impregnated with aqueous solution of KI and KOH .

4 Wh/TEDA impregnated carbon: Whetlerite impregnated with aqueous solution of TEDA.

5 ASZMT carbon: Activated carbon impregnated with ammonical solution of basic cupric carbonate, silver nitrate, basic zinc carbonate, ammonium heptamolybdate and aqueous solution of TEDA.

2.3. Surface Area Analysis

BET surface area and DR (Dubinin Radushkevich) micro pore volume of these carbon systems were determined by nitrogen up take at liquid nitrogen temperature using Autosorb 1C from Quantachrome USA .The values are tabulated in Table 1. Figures 1 and 2 represent the nitrogen adsorption isotherms of prepared systems.

2.4. Estimation of impregnants

Metal ions extracted in acidic and alkaline medium were estimated by atomic absorption spectrophotometic and titrimetric method. In Whetlerite systems Cu, Cr and Ag were extracted as $CuCl_2$, Na_2CrO_4 and $Ag_2S_2O_3$ using concentrated HCl, NaOH, and $Na_2S_2O_3$ respectively [7].

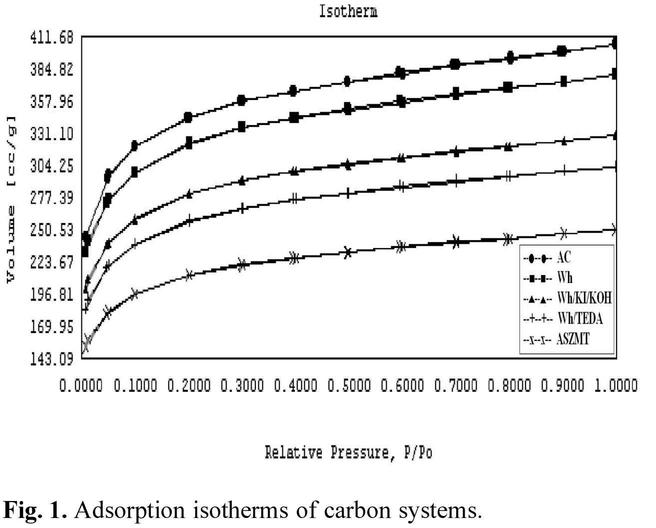

Fig. 1. Adsorption isotherms of carbon systems.

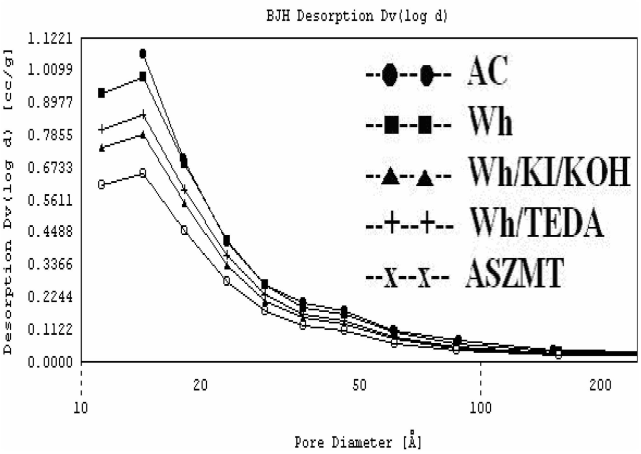

Fig. 2. Pore size distributions of carbon systems.

Copper, Silver, Zinc and Molybdenum from ASZMT carbon system were extracted with 20% HNO_3 and analyzed through atomic absorption spectrophotometer.

TEDA was extracted in methanol and determined quantitatively by using gas chromatography technique .The gas chromatograph (GC) was equipped with BP5 column and flame ionization detector (FID). The temperature of the oven, injection and detector were kept at 220, 160 and 280°C respectively.

Details on impregnants estimation are summarized in Table 2.

2.5. *Test rig for iodine generation*

An experimental test set up (Figure 3) was established for iodine vapour generation to study the breakthrough time of carbon bed and simultaneous measurement of iodine concentration. Iodine vapour has been generated by taking solid molecular iodine, AR grade in a round bottom flask maintained at 35°C using constant temperature water bath. Air was taken from the air cylinder (1) using rotameter (2) at a flow rate from 4 to 6 Lpm. A fixed amount of air (as per the requirement of air for I_2 vapour generation) measured through rotameter (3) was passed to round bottom flask (4) containing solid molecular iodine. The round bottom flask was kept in water bath (5) at 35±2°C to maintain a constant temperature throughout the experiment. This was mixed properly in a mixing chamber (6) using control valve (7) for the dilution of iodine vapours. Mixed air was then passed through rotameter (8) to the carbon column (9) at varying flow rates and iodine vapour breakthrough time was monitored by taking starch solution in a test tube (10) and the observation of blue colour ring developed at the upper layer of the solution was considered as breakthrough time.

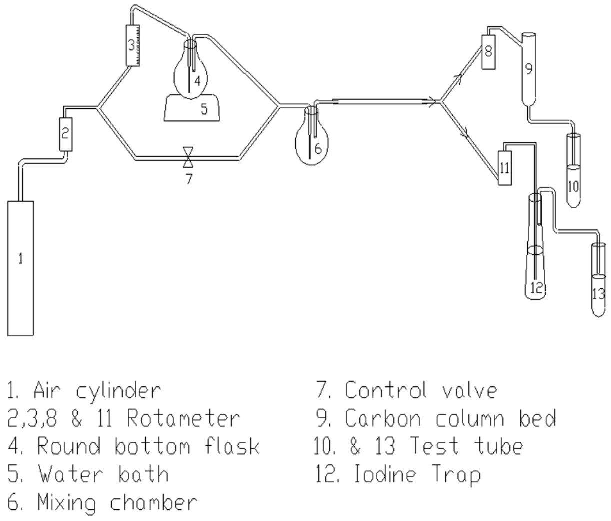

Fig. 3. Test rig used for iodine adsorption studies.

In order to measure the iodine concentration simultaneously a fixed volume [500 ml/min using rotameter (11)] of iodine-air mixture was passed through iodine trap (12) having 0.1 N sodium thiosulphate solution. This solution was kept in ice during experiment to avoid iodine escape. To further confirm the escape of iodine from iodine trap a test tube (13) containing starch solution was used, which could provide the blue colour ring development at the upper layer of the solution if iodine breaks through the iodine trap.

3. Results and Discussion

Military canister consists of particulate and gas filter,

Table 2. Estimation of Metal Ion Contents

Element (%)	Active carbon	Wh		Wh/KI/KOH		Wh/TEDA		ASZMT	
		Theo. (% w/w)	Cal. (% w/w)	Theo. (% w/w)	Cal. (% w/w)	Theo. (% w/w)	Cal. (% w/w)	Theo. (% w/w)	Cal. (% w/w)
Cu	Nil	6.5	6.3	6.5	6.1	6.5	6.0	6.5	6.2
Ag	Nil	0.22	0.19	0.22	0.18	0.22	0.18	0.22	0.18
Cr(VI)	Nil	3.0	2.5	3.0	2.6	3.0	2.4	Nil	Nil
Zn	Nil	Nil	Nil	Nil	Nil	Nil	Nil	6.5	6.0
Mo	Nil	Nil	Nil	Nil	Nil	Nil	Nil	3.0	2.5
TEDA	Nil	Nil	Nil	Nil	Nil	5.0	3.5	5.0	3.5
KI/KOH	Nil	Nil	Nil	2.5 each	--	Nil	Nil	Nil	Nil

Table 3. C T Values of Carbon Systems @ 3.0 Lpm Flow Rate

Bed-height (cm)	Space velocity (cm/sec)	C T Values (mg-min/L)				
		AC	Wh	Wh+KI+KOH	Wh+TEDA	ASZMT
2	31.83	242.0	176	154.	38	5
3	21.26	628	493	381	211	28
4	15.91	870	810	750	400	98
5	12.73	1225	1112	1002	580	160

Table 4. C T Values of Carbon Systems @ 4.0 Lpm Flow Rate

Bed Height (cm)	Space velocity (cm/sec)	C T Values (mg-min/L)				
		AC	Wh	Wh+KI+KOH	Wh+TEDA	ASZMT
2	42.44	132	100	72	26	2
3	28.32	350	227	182	88	16
4	21.22	600	478	304	224	54
5	16.97	965	621	485	297	140

Table 5. C T Values of Carbon Systems @ 5.0 Lpm Flow Rate

Bed Height (cm)	Space velocity (cm/sec)	C T Values (mg-min/L)				
		AC	Wh	Wh+KI+KOH	Wh+TEDA	ASZMT
2	53.05	82	55	32	20	1
3	35.37	308	210	175	65	11
4	26.52	465	390	272	190	18
5	21.22	686	570	440	250	29

provides protection against chemical, biological and nuclear contamination. Chemical contamination is removed by the filtration system via adsorption and chemical detoxification; however, the biological and nuclear contamination is removed by the particulate filter with the efficiency of 99.97% against 0.3 μ particles [1]. This clearly indicates that the nuclear contamination available in the form of particulates could only be removed by the filtration system. However, the nuclear contamination containing radioactive iodine [9] in the form of $I\text{-}I^{131}$ and CH_3I^{131} has not been taken care of. Therefore, for the removal of radio active iodine differently modified carbon samples were prepared, characterized and evaluated against I_2 vapours.

Active carbon of 1104 m^2/g surface area, when impregnated, showed the decrease in surface area (Table 1) from 1104 to 684 m^2/g. This may be due to the impregnants, which probably sit in the micro pore openings and meso pores. The micro pore and cumulative desorption pore volume also indicated the decrease in values in the case of the impregnated carbon samples, however, whetlerite showed higher value (0.43 cm^3/g) of cumulative desorption pore volume than the active carbon (0.34 cm^3/g). ASZMT carbon system showed the lowest values of surface area and pore volumes, which was due to the maximum percentage of impregnants (18.2% approximately). The whetlerite carbon, which is currently in use with indigenous NBC filtration systems, was taken as such, i.e., without further impregnation and it showed the maximum values of surface area and pore volumes amongst impregnated carbon systems (Table 1). Fig. 1 and 2 show the adsorption isotherms and BJH (Barret, Joyner and Halenda) pore size distribution curves of prepared carbon systems respectively. Fig. 2 also indicated the pore maxima to be 1.5 nm, which indicates the adsorbents to be micro porous. Table 2 indicates the concentration of metal ions extracted from the prepared carbon samples. It indicates that the experimental extracted metal contents are within the close agreement with the theoretical impregnation percentages..

Iodine breakthrough was studied for carbons of different bed lengths at different flow rates for initial concentrations in the range from 3 to 5 mg/L at 30±2°C. Table 3 to 5 describe the results. Space velocity [20], i.e., the volumetric feed flow rate per unit of reactor volume in chemical reactor was calculated for the studied reactor (carbon column) and the values are tabulated in Table 3 to 5. The carbon samples with different bed heights and flow rates were studied at space velocities ranging form 12.73 to 53.05 cm/sec. The results indicated that iodine CT (concentration x time) values decreased from 1225 to 686 mg-min/L with the increase in space velocity from 12.73 to 21.22 cm/sec respectively, which is quite evident from the fact that higher flow rate (space velocity) allows less contact time for adsorbate molecules to interact with adsorbent and getting adsorbed. However, for similar experimental conditions iodine CT values reduced from 160 to 29 mg-min/L for ASZMT carbon with the increase in space velocity from 12.73 to 21.22 cm/sec. The data in Tables 3~5 also indicated that iodine breaks through rapidly at higher space velocities with

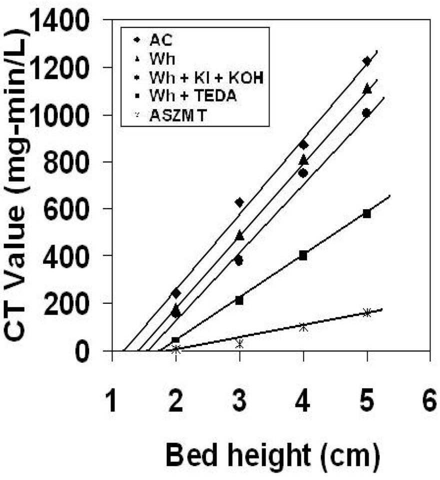

Fig. 4. Effect of carbon bed length on CT values at 3 Lpm flow rate.

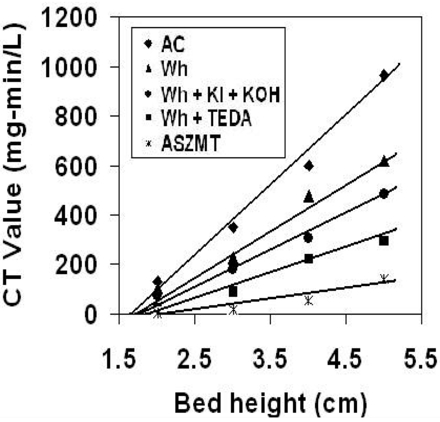

Fig. 5. Effect of carbon bed length on CT values at 4 Lpm flow rate.

all studied bed heights. ASZMT carbon system showed the least CT values, i.e., 1 to 160 mg-min/L for different carbon bed heights and space velocities. It was obviously because of low surface area of ASZMT carbon system, which decreases the break through time values against I_2 vapours and in turn decreases the CT values at constant concentration of I_2 vapours.

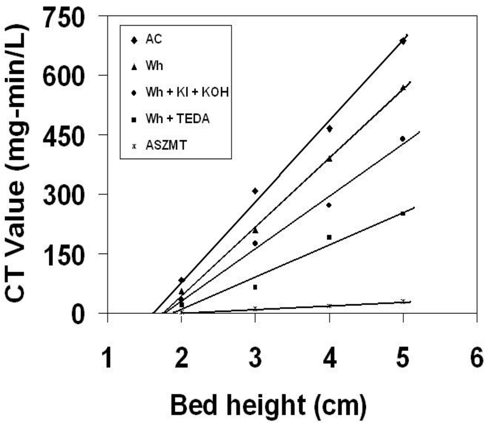

Fig. 6. Effect of carbon bed length on CT values at 5 Lpm flow rate.

In order to find out the dead layer (the minimum bed height of the carbon column required to get any protection because at dead layer bed height the adsorbate breaks through instantaneously), bed height of carbon column was plotted versus iodine CT values and these curves have been indicated in Fig. 4 to 6. This can be inferred from these curves that the dead layer of the carbon column was found to be increasing with the increase in flow rates (Table 6). Active carbon showed the dead layer values of 1.2, 1.6 and 1.7 cm at 3, 4 and 5 Lpm flow rates respectively, which is quite obvious due to the less contact time between adsorbate and adsorbent at higher flow rates. The dead layer values were also found to be increasing as we proceeded from active carbon to the impregnated carbons. It was due to the decrease in surface area values for active carbon (1104 m^2/g) to ASZMT carbon (684 m^2/g). Decrease in surface area, i.e., the decrease in available space with adsorbent to allow adsorbate molecules to occupy the adsorbent surface, decreases the adsorption capacity or breakthrough time values, and in turn increases dead layer values. The dead layer values were also found to be in close agreement with inverse proportionality with its surface area values. However, in any case the dead layer was not more than 2.0 cm, which indicated the bed height of carbon column to be always greater than 2.0 cm to have protection against I_2 vapours.

Although the literature [10] states that KI/KOH and TEDA impregnations increased the protection time offered by the adsorbents against radio iodine by isotopic exchange or complexing. But in the present study it was not observed because of the use of elemental I_2 vapours as simulant of radio iodine. The study clearly indicated that the protection

Table 6. Dead Layer Values for Carbon Systems at Various Flow Rates

Flow rate	Dead Layer (cm)				
	AC	Wh	Wh/KI/KOH	Wh/TEDA	ASZMT
3 LPM	1.2	1.4	1.5	1.7	1.8
4 LPM	1.6	1.7	1.7	1.8	1.9
5 LPM	1.7	1.8	1.8	1.9	2.0

against I_2 vapours is directly proportional to the surface area of the adsorbents under study; however, the interactions of I_2 vapours with TEDA to make complex cannot be ruled out. Further study to find out the effect of TEDA and KI/KOH impregnation on adsorbents is in progress and will be reported elsewhere.

4. Conclusion

Breakthrough behaviour of iodine vapours on carbon systems such as active carbon, whetlerite, whetlerite/TEDA, whetlerite/KI/KOH and ASZMT carbon systems was studied. Effects of various parameters such as bed height and flow rate were interpreted in terms of their I_2 CT values. CT values were observed to be increasing with the increase in bed height and decrease in space velocities. The protection time offered by the adsorbents were found to be directly proportional to their surface area values. The active carbon showed maximum protection at all bed heights and flow rates in comparison to all other impregnated carbon systems, showing that only physical adsorption is responsible for the removal of iodine vapours. The maximum dead layer was found to be 2.0 cm, which indicated the carbon bed height to be more than 2.0 cm for adequate protection by filtration system against I_2 vapours with studied carbon systems.

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