

Adsorption of dimethyl methylphosphonate on metal impregnated carbons under static conditions

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Abstract

Active carbon, grade 80 CTC, of surface area 1199 m²/g, 12 × 30 BSS particle size and coconut shell origin was impregnated (5%, W/W) with various impregnants such as Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate, Cu(II) 1,1,1-trifluoroacetylacetonate, 1-phenylbut-1,3-dione-2-oxime plus Cu(II) using incipient wetness technique. These impregnated carbons along with active carbon (Grade 80 CTC) and whetlerite were studied for the adsorption of dimethyl methylphosphonate (DMMP) at 33 ± 1 °C under static conditions. Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate impregnated carbon system showed highest uptake (68.5%, W/W) of DMMP amongst all the carbon systems, however, active carbon with higher surface area could adsorb 61.5% (W/W) of DMMP under same conditions. It indicated that the adsorption by Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate impregnated carbon was not only due to physisorption but chemisorption as well. Kinetics of adsorption was also studied and various parameters such as equilibration time, equilibration capacity, rate constant (*k*), diffusional exponent (*n*) and constant (*K*) were determined. Carbons with and without DMMP exposure were also studied using IR and TGA techniques. Reaction products were analyzed using gas chromatography coupled with mass spectrometry (GC/MS) and found to be methyl methylphosphonic acid (MMPA) and methylphosphonic acid (MPA) for Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate impregnated carbon.

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1. Introduction

Active carbon is well known for its capacity to remove toxic gases and vapours from contaminated air [1–3]. This characteristic of active carbon makes it more effective for use in various filtration systems of defence and industrial origin. Adsorbent used in these filtration systems mainly involves the processes of physical adsorption, chemical detoxification/degradation and chemisorption. Involvement of these processes depends on physical and chemical properties of the toxic chemicals, which are to be removed. For example, physical adsorption is the operating principle for the removal of high molecular weight and low volatile chemicals {persistent chemical warfare (CW) agents, i.e., blister and nerve agents} in filtration systems. For the other category, i.e., low molecular weight and highly volatile

toxic chemicals (non-persistent CW agents), a reactive carbon is needed, which can perform two activities; one is the physical adsorption of the toxic chemical and second one is the degradation of the physisorbed vapours by chemical reactions. In order to make the carbon reactive towards non-persistent CW agents, it is impregnated with metal salts and is called impregnated carbon. One such impregnated carbon developed long back is whetlerite, i.e., active carbon impregnated with Cu(II), Cr(VI) and Ag(I) [4–8]. This carbon was used for the reactive removal of non-persistent chemical warfare agents like cyanogen chloride, phosgene and hydrogen cyanide by converting them into non-toxic products, however, the protection against persistent (blister and nerve) agents was based on physical adsorption. It is felt that these physisorbed toxic gases may desorb and cross contaminate the environment if used filtration systems (NBC canisters and filters) are thrown carelessly or are not disposed off properly. This situation needs the development of a suitable impregnated carbon system, which can perform in situ degradation (physisorption followed by chemisorption

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of the adsorbate) of persistent CW agents within the filtration systems.

Very scanty literature is available for in situ degradation of persistent CW agent. Karwacki et al. [9] have studied the adsorption equilibria of sarin on activated carbon at ultra low relative pressure. Karwacki et al. [10] has also discussed the effect of temperature on the decomposition of sulphur mustard on activated carbon with and without co-adsorbed water. Templeton and Weinberg [11] described the adsorption and decomposition of DMMP on aluminium oxide surface at temperature ranged from 200 to 673 K. Raza et al. [12] studied the hydrolysis of phosphofluoridates by Cu(II) diamine complexes in solutions. Ekerdt et al. [13] discussed the decomposition chemistry of organophosphorus compounds interacting with metal and metal oxide surfaces. He has also highlighted on significant research directions for surface chemical sciences, surface reaction chemistry, solid-state synthesis and organometallic cluster chemistry. Work has also been carried out for the infrared study of adsorbed organophosphorus on silica [14]. Attempts were also made by Cao et al. [15] to study the higher temperature thermo catalytic decomposition of dimethyl methylphosphonate on activated carbon to carbon dioxide, methanol and phosphorus pentoxide.

Chagger et al. [16] in 1995 discussed the kinetics of adsorption and diffusion characteristics on carbon molecular sieves using Ficks diffusion laws and linear driving force (LDF) mass transfer model. Kinetics of adsorption and diffusion over impregnated carbon system can be studied under two conditions; one is dynamic (continuous flow of gas) and the other static (no flow of gas). Adsorption under static conditions makes the adsorbate to stay with adsorbent significantly for longer time in comparison to the adsorption under dynamic conditions. Therefore, the adsorption of CW agents on carbons under both static and dynamic conditions is equally important to understand the mass transfer phenomena, mode of diffusion, adsorption characteristics and chemical degradation.

In the present study, i.e., static adsorption of DMMP over metal impregnated carbons, DMMP has been used as a simulant [13–15] of nerve agents as it has volatility and water solubility similar to that of sarin. As the present study deals with the adsorption of DMMP on carbon systems, therefore, it is also worth mentioning that adsorbed DMMP on carbon is more stable than adsorbed sarin because it does not have highly reactive group as available with sarin (P–F group). In order to perform the static adsorption impregnated carbon systems were prepared by impregnating high surface area active carbon with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate, Cu(II) 1,1,1-trifluoro acetylacetonate and 1-phenylbutane-1,3-dione-2-oxime plus Cu(II). These impregnated carbon systems along with active carbon and whetlerite were studied for the adsorption of DMMP under static conditions.

2. Experimental

2.1. Materials

Active carbon, grade 80 CTC of 12×30 BSS particle size, coconut shell origin and $1199 \text{ m}^2/\text{g}$ surface area

(N2BET) was obtained from M/S Active Carbon India Ltd., Hyderabad, India. Whetlerite was also obtained from M/S Active Carbon India Ltd., Hyderabad, India. The used whetlerite, an impregnated carbon system has copper (6.0%), chromium (2.5%), silver (0.2%), sodium hydroxide (2.0%) and pyridine (2.5%). DMMP was of AR grade from Aldrich (USA). Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate and Cu(II) 1,1,1-trifluoroacetylacetonate were of Lancaster, England. 1-phenylbutane-1,3-dione-2-oxime was synthesized. For synthesis, at $10\text{--}15^\circ\text{C}$ 100 g benzoylacetone was taken in 310 mL of acetic acid then 20 g of sodium nitrite was added to it slowly with stirring. The temperature of the mixture was maintained below 20°C for 2 h then the mixture was poured into cold water. The compound was filtered and finally re-crystallized from ethanol. The melting point of the oxime was found to be $124\text{--}126^\circ\text{C}$.

2.2. Preparation of carbons

The active carbon was impregnated with (5% w/w) of Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate, Cu(II) 1,1,1-trifluoroacetylacetonate and Cu(II) plus 1-phenylbutane-1,3-dione-2-oxime to obtain Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C, Cu(II) 1,1,1-trifluoro acetylacetonate/C and Cu(II) plus 1-phenylbutane-1,3-dione-2-oxime/C systems respectively. Aqueous solutions of the impregnants were used for the impregnation and the technique used for this was incipient wetness technique [1,17]. The impregnated carbons were dried at 110°C for 6 h, cooled in desiccator and finally stored in airtight bottles.

2.3. Characterization of carbons

Copper and chromium metal ions were extracted from carbon systems in acidic and basic medium and determined iodometrically [18]. Silver was extracted from impregnated carbon with sodium thiosulphate and determined using atomic absorption spectrophotometer. Percentage of extracted metal ions was found to be in close agreement (Table 1) with its theoretical values, i.e., the amount of metal in impregnated compounds. Surface area (N_2 BET), micropore volume (DR method), pore size distribution (BJH) and total pore volume of these carbons was determined by nitrogen uptake at liquid nitrogen temperature using Autosorb 1C from Quantachrome, USA. The results are tabulated in Table 2 and Fig. 1 represents the BJH pore size distribution and cumulative pore volume.

Table 1
Details of impregnants loaded on carbon systems

Carbon system	Metal impregnants	Impregnants (%)	
		Theoretical	Observed
Active carbon	No impregnant	Nil	Nil
Cu trifluoro acetylacetonate/C	Copper	0.86	0.84
Cu hexafluoro acetylacetonate/C	Copper	0.66	0.66
Cu plus oxime/C	Copper	2.87	2.80
Whetlerite	Copper	6.00	5.85
	Chromium	2.50	2.44
	Silver	0.20	0.20

Table 2
Kinetic parameters for adsorption of DMMP on carbons

Type of carbon system	Equilibration time (h)	Equilibration capacity (mg/g)	Rate constant (k) (h^{-1})	Constant (K) (h^{-1})	Diffusional exponent (n)	Micro pore volume (cc/g)	Total pore volume (cc/g)	Surface area (m^2/g)
Active carbon	390	615	1.01×10^{-2}	1.89×10^{-2}	0.70	0.68	0.75	1199
Cu trifluoro acetylacetonate/C	398	584	1.00×10^{-2}	2.10×10^{-2}	0.71	0.62	0.64	1090
Cu hexafluoro acetylacetonate/C	435	685	0.80×10^{-2}	1.24×10^{-2}	0.80	0.65	0.69	1156
Cu plus oxime/C	392	478	1.20×10^{-2}	2.51×10^{-2}	0.67	0.55	0.57	970
Whetlerite	447	505	1.01×10^{-2}	2.68×10^{-2}	0.64	0.56	0.58	1005

2.4. Adsorption of DMMP

In order to carry out the adsorption of DMMP under static conditions, 400 mg each of carbon samples were taken separately in Gooch crucibles and placed in a desiccator in which 2.0 ml of DMMP was placed in the bottom of desiccator. To maintain constant temperature, the desiccator was housed in an environmental chamber kept at $33 \pm 1^\circ\text{C}$. This chamber was used not only to control the temperature but also to house the weighing balance. Vapour pressure of DMMP in the desiccator was measured and found to be 1.3 mm Hg at 33°C . Moisture-free air was not used for the experiments. The concentration of gas was considered to be constant at atmospheric pressure in the desiccator. As the adsorption of DMMP by the carbon starts, it causes the depletion in vapour phase concentration of DMMP in the desiccator. The depletion in concentration is compensated by liquid phase DMMP, which was placed in the bottom of the desiccator. Therefore, the concentration of DMMP in the desiccator remains constant and it ensures a continuous supply of DMMP to the adsorbent. The kinetics of adsorption of DMMP was studied by monitoring the percentage of weight gain every hour as shown in Fig. 2.

2.5. TGA, GC/MS and IR study

Thermograms for unexposed and DMMP exposed carbon systems were then recorded from 0 to 650°C in air using thermogravimetric analyzer, TGA-2950 from TA Instruments, USA. The initial sample weight was always 10 mg and the heating rate was $10^\circ\text{C}/\text{min}$. DMMP exposed carbons with and without metal salts were extracted with dichloromethane for 2 h, extracts were purged by nitrogen gas to increase the concentration of products. These concentrated reaction products were silylated and analyzed by GC-MS. For IR analysis 5 mg of unexposed and DMMP exposed carbon sample was mixed with 200 mg of potassium bromide, ground to make pellets, dried and finally recorded IR spectra.

3. Results and discussion

To illustrate the kinetics of adsorption of DMMP, percentage weight gain of adsorbate was plotted versus time (t) and represented graphically in Fig. 2. Since moisture free air was not used to monitor the kinetics of adsorption of DMMP the possibility of co-adsorption of atmospheric moisture cannot be ruled out. However, the co-adsorption of water will be insignificant and will not affect the DMMP adsorption due to very little influence of humidity on adsorption of DMMP [19].

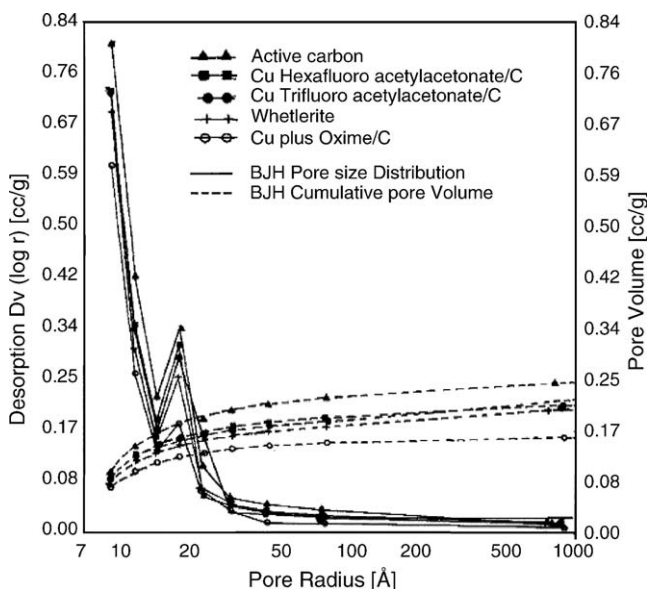


Fig. 1. Pore size distribution and pore volume of carbon systems.

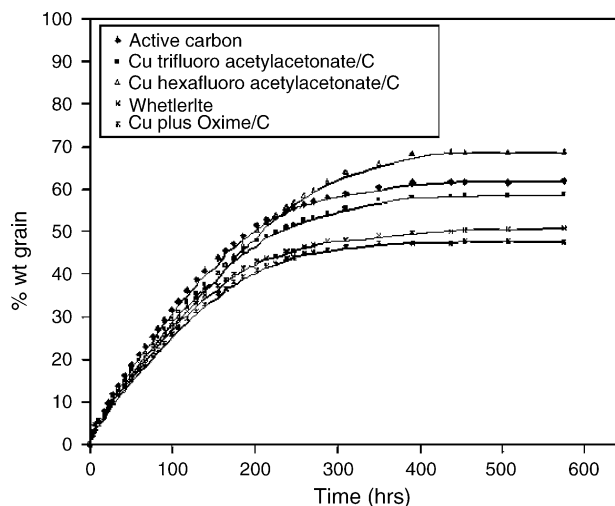


Fig. 2. Kinetics of adsorption of DMMP on carbons.

Fig. 2 shows similar shapes of DMMP adsorption uptake curves and different adsorption rates for studied carbon systems. Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system showed maximum DMMP uptake amongst other systems. Initially rate of adsorption of DMMP by this carbon is observed to be slow, which increases with time and after 230 h it seems to be fastest amongst other carbon systems. Fig. 2 was used to compute the equilibration time (the time at which the adsorption ceases, i.e., no change in weight gain with respect to time) and equilibration capacity (amount of adsorbate in mg/g of adsorbent at equilibration time) the values are tabulated in Table 2. Equilibration time was found to be increasing for the impregnated carbon than active carbon. It was because of impregnants, which work as a barrier and resist the movement of adsorbate molecules [20]. The impregnants also react with physisorbed DMMP and give rise to the formation of products confirmed by GC/MS after extraction using dichloromethane. The reaction products remain on the surface of impregnated carbon and poison it for further adsorption. Whetlerite showed the highest value (447 h) of equilibration time amongst all impregnated carbon systems. Probably it was because of higher percentage of impregnants in whetlerite (13–14% w/w) than other impregnated carbon systems (5% w/w).

Active carbon of 1199 m²/g surface area when was impregnated with appropriate impregnants to prepare impregnated carbon systems such as Cu hexafluoroacetylacetonate/C, Cu trifluoroacetylacetonate/C, Cu plus oxime/C showed decrease in surface area (1156–970 m²/g, Table 2). It was because of impregnants, which occupy the mesopores and can block the pore opening of micropores. This leads to decrease in surface area and change in porosity. Decrease in surface area simply leads to decrease in adsorption potential, i.e., equilibration capacity. The equilibration capacity for Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C (68.5%, W/W) was found to be higher than active carbon (61.5% W/W), however, the surface area for Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system (1156 m²/g) was lesser than active carbon (1199 m²/g). This interesting behavior of high adsorption potential with lesser surface area indicates the adsorption by Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system was not only due to physisorption but also involved chemisorption, where the physisorbed DMMP molecules diffuse to the chemisorption sites and react with the impregnants, ultimately resulting in the increased adsorption potential.

The study indicates that the transport of the DMMP into carbon is a complex process. It is quite evident from the fact that active carbon contains wide pore size distribution, which makes the analysis of adsorption kinetics more complex. The adsorption process involves diffusion in slit shaped micro pores with pores widths considerably smaller than the mean free path of the gas molecules at atmospheric pressure. It is likely that processes such as molecular diffusion, Knudsen diffusion, surface diffusion, diffusion in micro pores and the chemical interaction of the adsorbate molecules with the functional groups in active carbon and the impregnants in impregnated carbons could all make contributions to the adsorption of DMMP on carbon systems.

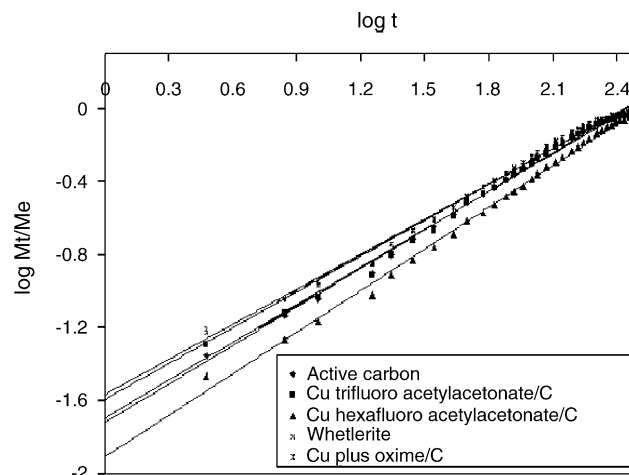


Fig. 3. Kinetics of diffusion of DMMP on carbons.

Modeling of kinetic process being difficult due to wide pore size distribution, the two simple approaches are to use either Ficks diffusion laws for homogeneous materials or to describe the process by Phenomenological model. Although, the particles under study are not homogeneous and spherical, if we assume surface concentration of gas to be constant and that diffusion is controlled by the concentration gradient through the granule then the kinetics of the diffusion can be expressed by the following empirical diffusion equation [16,21]:

$$M_t/M_e = Kt^n \quad (1)$$

where, M_t = gas uptake at time t , M_e = gas uptake at equilibrium, K = constant, t = time and n = diffusional exponent.

A graph of $\log M_t/M_e$ against $\log t$ (Fig. 3) found to be a straight line with gradient n . It describes the kinetics of DMMP diffusion on carbons. Diffusional exponent (n) values (Table 2) were found to be in between 0.64 and 0.8. Values of n being between 0.5 and 1.0 indicated the diffusion mechanism to be anomalous. The values for constant K , adsorbate–adsorbent interaction coefficient was determined from the intercept of straight lines on Y -axis. K represents the interaction between adsorbate and adsorbent, i.e., higher the K -values higher will be the interaction of adsorbate with adsorbent. In present studied systems, Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system showed the lowest value of K ($1.24 \times 10^{-2} \text{ h}^{-1}$) while other systems showed small differences in K -values and may be within the experimental precision. Lowest value of K with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system represented the minimum interaction of DMMP with the system but contrary it showed maximum adsorption among all studied systems. It was probably because of the adsorption behavior of Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system. As Fig. 2 showed that the adsorption of DMMP by Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system was almost comparable to other systems up to 170 h and after that it proceeded with faster adsorption rate and even crosses active carbon (at 230 h) which has higher surface area than it. This indicated that initially DMMP is physically adsorbed on Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system followed by

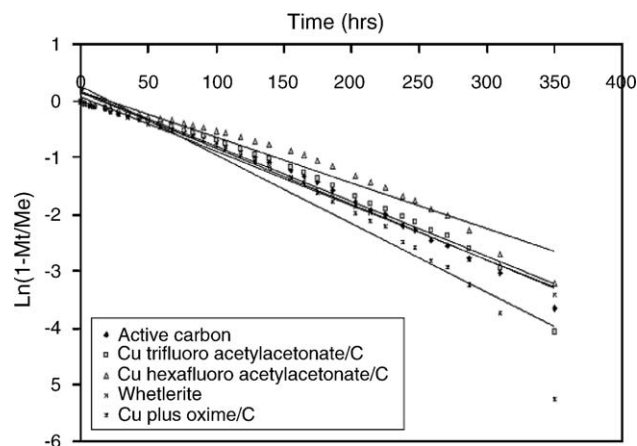


Fig. 4. Kinetics of adsorption of DMMP on carbons.

involvement of chemisorption process which leads to the highest uptake of DMMP, i.e., the interaction of adsorbate (DMMP) with adsorbents (Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system) started at higher t values (prolonged time) while the K -values determined from Fig. 3 were more or less the result of adsorption kinetics at lower t -values. In order to understand the diffusion process, pore size distribution of the adsorbents is very important. The pore size distribution of all the carbon system was studied and observed the pore maxima at 0.9 nm, which was found to be same even in the impregnated carbon system. However, the intensity reduced in impregnated carbon systems indicated the reduction in pore volume. The detail on pore volume has been provided in Table 2. The reduction in the pore volume is proportional to the impregnants and indicates that the adsorption rate was higher initially in the active carbon due to favorable porous structure for physical adsorption. The latter decreased in the impregnated carbon systems due to the changed pore structure initially, however, it was enhanced by the chemical interaction with impregnants in the later stages of adsorption.

The gas uptake into carbon particles may be considered as a pseudo-first order mass transfer between the gas phase and the carbon adsorption sites [16,21]. The following phenomenological model, which is equivalent to a linear driving force mass transfer model, can represent the rate of uptake of DMMP.

$$M_t/M_e = 1 - e^{-kt} \quad (2)$$

where, k is rate constant.

Plots of $\ln(1 - M_t/M_e)$ against time t (Fig. 4) gave a straight line which clearly indicated that the adsorption of DMMP on studied systems follows LDF mass transfer kinetic model. The adsorption kinetics can be compared in terms of the rate constant (k), which indicates the rate of adsorption of DMMP as the system approaches to equilibrium. Rate constant, k can either be determined from the gradient of the kinetic plot as shown in Fig. 4 or by fitting the adsorption uptake curves to Eq. (2). The rate constant k was determined using Fig. 4 and values are summarized in Table 2. Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system indicated the lowest value of rate constant, i.e., $0.8 \times 10^{-2} \text{ h}^{-1}$. However, the rate constant values for other systems were found to be comparable

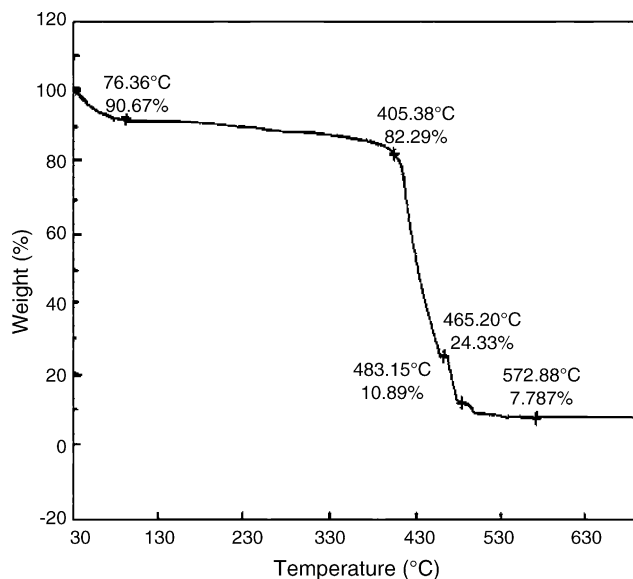


Fig. 5. Thermogram for Cu hexafluoroacetylacetonate/C.

and within the experimental precision (Table 2). Lowest value of k with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system was because of its adsorption behavior. As, the k -values were determined using the gradient of kinetic plots of Fig. 4 which more or less represented the adsorption kinetics at lower t -values while Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system proceeded with faster DMMP up take at higher t values, i.e., at lower t -values DMMP is physisorbed on Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system but at higher t -values it involved chemisorption as well. Higher equilibration time with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system also lowered the rate constant.

As, Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system showed maximum adsorption potential for DMMP among all studied systems. Therefore, it was studied (before and after the adsorption of DMMP) for TGA, GC/MS and IR studies. Thermograms for unexposed and DMMP exposed carbon samples were recorded in air. Unexposed active carbon showed higher stability of carbon (up to 450 °C) than other unexposed impregnated carbon systems (up to 400 °C). A little less stability of impregnated carbon was due to the presence of metal in impregnated carbons, which seemed to facilitate the faster burning of impregnated carbon. Figs. 5 and 6 show the thermograms of unexposed and DMMP exposed Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate /C system.

Thermograms for DMMP exposed carbon samples showed that co-adsorbed moisture evolved out completely at 100 °C followed by desorption of adsorbed DMMP up to the temperature of 250 °C. Thermal stability of DMMP exposed impregnated carbon was observed to be 516 °C (Fig. 6), which is significantly higher in comparison to the thermal stability of unexposed impregnated carbon (400 °C, Fig. 5). This observation indicated that adsorbed DMMP has increased the thermal stability of carbon system.

Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system showed 685 mg/g as equilibrium capacity for DMMP adsorp-

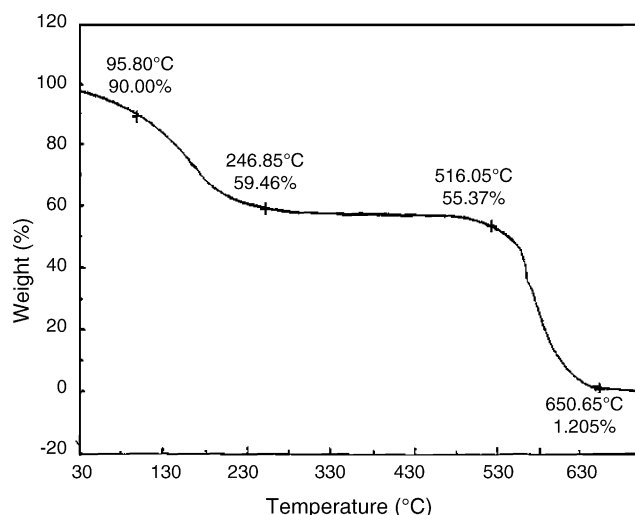


Fig. 6. Thermogram for DMMP exposed Cu hexafluoroacetylacetonate/C.

tion, i.e., 100 mg of DMMP equilibrated sample of Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system contains 40 mg of DMMP. Thermogram of unexposed Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system (Fig. 5) showed 18% weight loss up to 405 °C, while DMMP exposed Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system (Fig. 6) showed 41% weight loss up to 405 °C. It clearly indicated that 23 (41–18) mg of DMMP has come out from 100 mg of DMMP exposed Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system up to 405 °C, while remaining 17 (40–23) mg of DMMP was still available with carbon up to 405 °C. Therefore, DMMP adsorption over Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system involved both physisorption and chemisorption processes, i.e., physisorbed DMMP desorbed on heating, while chemisorbed DMMP made a stable complex with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate and remained with carbon even at higher temperatures (516 °C). IR data also supported the interaction of DMMP on active carbons with and without impregnants, where frequency of P=O group has been observed in the region (1233–1226 cm^{-1}) against the P=O of vapour phase DMMP at 1275 cm^{-1} .

DMMP exposed carbons were studied for the reaction products after extracting from a fixed amount of carbon with dichloromethane and analyzing using GC/MS technique. The process of degradation of DMMP on impregnated carbon systems was found to be very slow. It was because of the reason that DMMP does not have highly reactive group to react with impregnants and produce products to the greater extent. GC profile of GC/MS study showed that products were in the range of 1–2% of total adsorbed DMMP with all carbon systems except active carbon, which did not show any significant degradation. Peak intensity of products from GC profile of GC/MS study also showed the maximum degradation with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system. It indicated that Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system might be the potential system for in situ degradation of DMMP amongst the studied impregnated carbon systems.

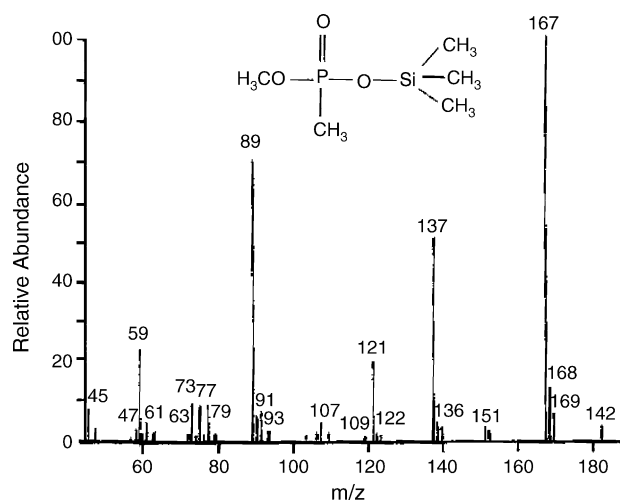


Fig. 7. Mass spectra of silylated methylmethphosphonic acid.

All the carbon systems except active carbon gave methyl methylphosphonic acid (MMPA) and methylphosphonic acid (MPA) as the reaction products and Scheme 1 represents the reactions. Figs. 7 and 8 describes the mass spectra of extracted reaction products, i.e., MMPA (182, 167, 137, 89, 73, and MPA (240, 225, 147, 133, 105, 73) respectively. These spectra were well matched with the standard spectra available in the existing libraries (NIST 02 and the library which has been generated by our laboratory using known compounds) of the instrument (GC/MS).

Infrared spectra of carbon systems are always complex due to the presence of various surface functional groups and co-adsorbed water. Figs. 9 and 10 shows the IR spectra of active carbon and Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system (alone and after adsorption of DMMP), respectively. All the DMMP exposed carbon systems gave additional peaks in comparison to unexposed carbon systems at 1410, 1233, 1034,

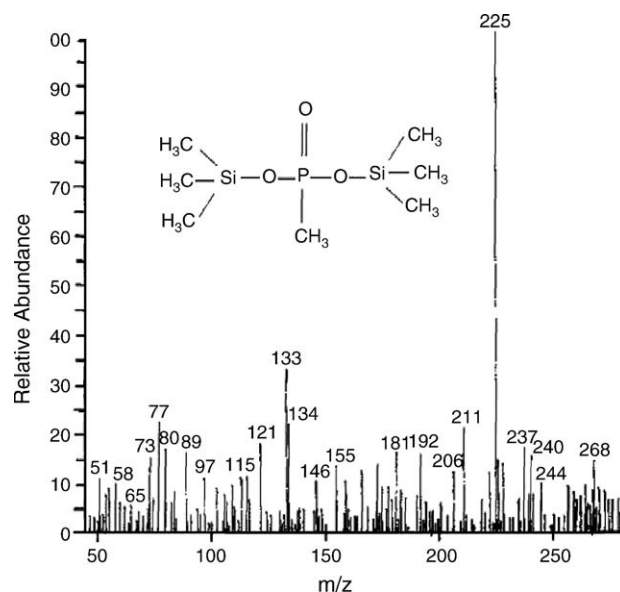
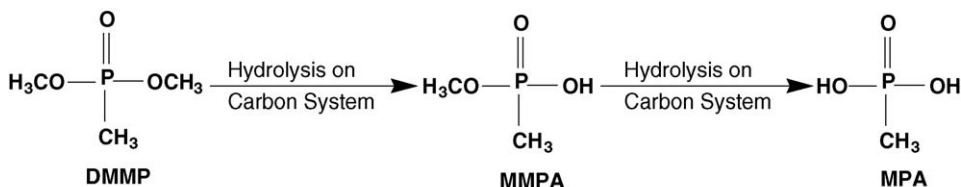


Fig. 8. Mass spectra of silylated methylphosphonic acid.



Scheme 1.

922 and 819 cm^{-1} , which indicated the presence of DMMP on the carbon surface. Active carbon has various acidic functional groups such as carbonyl, lactonic, phenolic, etc. These groups are acidic in nature and attract electron rich moieties. Due to differences in electro negativity of oxygen and phosphorus atom the P=O group of DMMP develops some polarity, i.e., more electron density on oxygen atom of DMMP. Therefore, the shift of the P=O stretching mode for vapour phase DMMP (1275 cm^{-1}) to adsorbed DMMP on carbon (1226 cm^{-1}) indicated that DMMP

adsorbed through an interaction of the P=O group with the surface functional groups of carbon (Fig. 9). Similar observation was also reported by Kanan and Tripp [14] for the adsorption of DMMP on silica. In case of impregnated carbon P=O group of DMMP also interacts with the copper of impregnated carbon systems which is supported by the absorption peak in the almost same position, i.e., 1233 cm^{-1} (Fig. 1) for P=O group with Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate impregnated carbon. This interaction leads to the development of slightly positive charge on phosphorus atom of DMMP, which react with water and give rise to the formation of reaction products (MMPA & MPA). As active carbon did not give DMMP products it indicated that the interaction of DMMP with surface functional groups of active carbon is not sufficiently enough to form the products. Investigations indicated that Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system showed highest intensities of IR peaks amongst all the DMMP exposed carbons, which highlighted the highest amount of DMMP on carbon. Therefore, It can be inferred from this observation that the interaction of DMMP is not only through surface functional groups on carbon surface but also through coordination with copper moiety of Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system. Higher intensities of peak at 3440 cm^{-1} with DMMP exposed carbon systems indicated the presence of excess -OH groups. Probably it was due to co-adsorbed moisture or the hydrolysis product of DMMP, i.e., methyl methylphosphonic acid and methylphosphonic acid.

In order to understand the highest DMMP adsorption potential shown by Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system, the C=O stretching frequencies were studied for the Cu(II) complexes of acetylacetonate, 1,1,1-trifluoroacetylacetonate and 1,1,1,5,5,5-hexafluoroacetylacetonate through IR. These frequencies were observed to be at 1577, 1610 and 1647 cm^{-1} for Cu(II) acetylacetonate, Cu(II) 1,1,1-trifluoroacetylacetonate and Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate respectively. This indicated that copper is strongly coordinated with carbonyl group in acetylacetonate complex and very weakly bonded in 1,1,1,5,5,5-hexafluoroacetylacetonate complex. This is quite evident due to the presence of highly electronegative fluorine atom in the later which withdraws electrons towards carbon of carbonyl group rendering the carbonyl group to be less effective for coordination with copper moiety in the copper complex. Therefore, it can be inferred from this study that DMMP can be chemisorbed in the increasing order in the Cu(II) complexes of acetylacetonate, 1, 1, 1-trifluoroacetylacetonate and 1, 1, 1, 5, 5, 5-hexafluoroacetylacetonate as the copper moiety is more free in the later than others for coordination with P=O bond of DMMP.

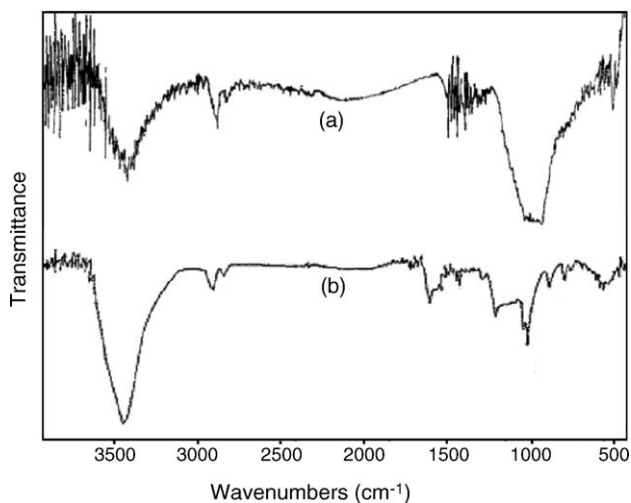


Fig. 9. IR Spectra of DMMP. (a) Unexposed. (b) Exposed active carbon.

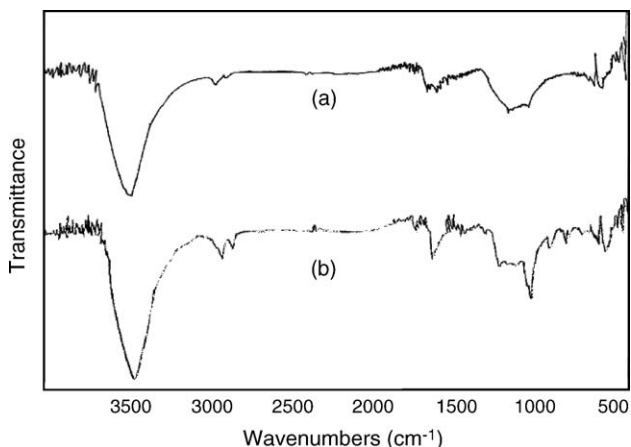


Fig. 10. IR Spectra of DMMP. (a) Unexposed. (b) Exposed Cu hexafluoroacetylacetonate/C.

4. Conclusion

DMMP adsorption on carbons both active and impregnated was studied under static conditions and results were also interpreted using empirical diffusion equation, phenomenological model, TGA, IR and GC/MS studies. It was observed that Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system showed the highest uptake (68.5% w/w) of DMMP amongst other impregnated carbons, even higher than active carbon (61.5%). The diffusion of DMMP in the carbons was found to be anomalous based on values of n (diffusional exponent) observed to be in the range 0.64–0.8. The study also indicated that Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system is a suitable system for the adsorptive removal of DMMP, a nerve agent stimulant from the environment. TGA study indicated that chemisorbed DMMP stabilizes the Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate/C system thermally up to a very high temperature (516 °C). IR study also confirmed the chemical interaction of DMMP with the copper moiety of the impregnated carbon. This interaction leads to the degradation of DMMP to the extent of 2.0% via the development of slightly positive charge on phosphorus atom of DMMP favorable for hydrolysis to give rise to the formation of reaction products (methyl methylphosphonic acid and methylphosphonic acid) on the surface of impregnated carbons.

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