Kinetics of In-situ Degradation of Nerve Agent Simulants and Sarin on Carbon with and without Impregnants

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Abstract

Room temperature kinetics of degradation of nerve agent simulants and sarin, an actual nerve agent at the surface of different carbon based adsorbent materials such as active carbon grade 80 CTC, modified whetlerite containing 2.0 and 4.0 % NaOH, active carbon with 4.0 % NaOH, active carbon with 10.0 % Cu (II) ethylenediamine and active carbon with 10.0 % Cu (II) 1,1,1,5,5,5-hexafluoroacetylacetonate were studied. The used adsorbent materials were characterized for surface area and micropore volume by N_2 BET. For degradation studies solution of simulants of nerve agent such as dimethyl methylphosphonate (DMMP), diethyl chlorophosphate (DEClP), diethyl cyanophosphate (DECnP) and nerve agent, i.e., sarin in chloroform were prepared and used for the uniform adsorption on the adsorbent systems using their incipient volume at room temperature. Degradation kinetics was monitored by GC/FID and was found to be following pseudo first order reaction. Kinetics parameters such as rate constant and half life were calculated. Half life of degradation with modified whetlerite (MWh/NaOH) system having 4.0 % NaOH was found to be 1.5, 7.9, 1206 and 20 minutes for DECnP, DEClP, DMMP and sarin respectively. MWh/NaOH system showed maximum degradation of simulants of nerve agents and sarin to their hydrolysis products. The reaction products were characterized using NMR technique. MWh/NaOH adsorbent was also found to be active against sulphur mustard.

Keywords : Adsorption, Degradation, Impregnation, Kinetics, Porous Material, Surface Reactions

1. Introduction

Nerve agents are well known for their toxicity due to the inhibition of the enzyme acetylcholinesterase and use as chemical warfare agents. This enzyme affects the fission of acetylcholine, which is the chemical transmitter of a stimulus between nerve cells [1]. If, acetylcholine is no longer decomposed, the receiving nerve and muscle cells are continuously stimulated. This disturbance of the neural transmission finally leads to the death of the victim.

In order to provide protection against the toxic agents, filtration systems have been employed for the purification of air and water streams [2-4]. In filtration systems activated carbon is used which is a well known universal adsorbent due to its high adsorption capacity [2-8]. Adsorption capacity of active carbon is due to its wide pore size distribution, i.e., availability of micro, meso and macro pores. Micro pores of active carbon are mainly responsible for the adsorptive removal of chemical vapors of organic nature such as blister and nerve agents due to physisorption. Physisorbed blister and nerve agents remain as such on the carbon surface with little hydrolysis and pose the danger of

cross contamination due to desorption [2]. However, question often arises for the safe disposal of carbon filters used against nerve or blister agents. Therefore, the degradation of nerve and blister agents on the surface of adsorbent materials is of great interest in connection with safe disposal of used NBC filtration systems. The problem of safe disposal and handling can be overcome if carbon is preimprgnated with some catalytic materials to add chemical degradation property to the physisorption capacity of carbon.

ASC Whetlerite was developed in world war II, which is a carbon, impregnated with metal salts of Cu(II), Cr(VI) and Ag(I) [2]. This impregnated carbon is used in NBC filtration system for the removal of persistent and non-persistent 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 nonpersistent 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, 9-16]. Ideally the filtration systems should be such that 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 exits a requirement of development of adsorbent material for the filtration systems capable of degrading all type of CW agents chemically into non toxic products.

Very scanty literature is available for in-situ (physisorption followed by chemisorption of the adsorbate) degradation of nerve agents. Smisek and Cerny [8] has mentioned about a number of chemical effects upon warfare agents induced by inorganic impregnations. Most of these chemical interactions between adsorbent and agent involve a surface reaction, consuming the impregnation material. Raza *et al.* [17] has studied the hydrolysis of phosphofluoridates by Cu(II) diamine complexes in solutions. Augustinson *et al.* [18] has described the effectiveness of Cu(II), Ni(II), Ag(I), Au(III) and Pd(III) salts in accelerating the hydrolysis of phosphono-cyanidate in solutions. Kuiper *et al.* [19] has described the adsorption and decomposition of sarin on γ-alumina. Courtney *et al.* [20] has discussed the effect of metal chelate compounds as catalysts in the hydrolysis of isopropylmethylpho-sphonofluoridate and diisopropylphosphorofluoridate in solutions. Epstein *et al.* [21] has studied the kinetics of some metal ion catalyzed hydrolysis of sarin at 25 °C. Study for adsorption and decomposition of dimethyl methylphospho-nate on an aluminium oxide surface has been investigated with inelastic electron tunneling spectroscopy [22].

Decontaminating adsorbent can degrade CW agents by variety of reactions, such as oxidation, hydrolysis, elimin-ation, addition and dealkylation [23]. However, appropriate reaction needs to be chosen for the development of suitable and ideal adsorbent material for NBC filtration system. Blister and nerve agents are succeptible to hydrolysis and oxidation. Both the process require additional reactants, i.e., water and oxygen, which are profusely present in the ambient air. Hydrolysis is faster than oxidation at room temperature, thus making hydrolysis more promising with respect to decontaminating adsorbents [19]. Another factor is that nerve agents are highly prone to hydrolysis. Hydrolytic degradation, therefore, was considered to design and develop adsorbents for in-situ degradation of physisorbed nerve agents on carbon surface. Organophosphorus compounds such as dimethyl methylphosphonate (DMMP), diethyl chlorophosphate (DEClP) and diethyl cyanophosphate (DECnP) were chosen as simulants of nerve agents on the basis of literature [23-27], their structure resemblance and closer molecular dimensions to the nerve agents (calculated using method reported elsewhere [7]).

In the present study attention is directed towards the development of a carbon based adsorbent material capable of in-situ degradation of nerve agent simulants and sarin, an actual nerve agent. For this, different adsorbent materials such as modified ASC Whetlerite containing 2.0 and 4.0%, NaOH, Cu(II)1,1,1,5,5,5-hexafluoro acetylacetonate (10%) impregnated carbon and Cu(II) ethylenediamine (10%) impregnated carbon were prepared. These impregnated adsorbent systems were studied for their detoxification capability against nerve agent simulants such as dimethyl methylphosphonate, diethyl chlorophosphate, diethyl cyano-phosphate and sarin, the actual nerve agent. Kinetics parameters such as rate constant and half life were calculated using the first order rate equation and the degradation products were characterized using NMR technique.

2. Experimental Section

2.1. Materials

Active carbon, grade 80 CTC of 20×30 BSS particle size, coconut shell origin and 1337 m^2/g surface area (N_2BET) was procured from M/s Active Carbon India Ltd., Hydera-bad. Sarin was provided by Process Technology Develop-ment Division of our laboratory. DMMP, DECnP and DEClP were of AR grade from Fluka, Lancaster, and Acros respectively. *Caution: All discussed nerve agent simulants and sarin are extremely toxic and potent acetylcholine esterase inhibitor, therefore, they must he handled by trained personnel using proper protective gear and keeping safety procedures in mind.*

2.2. Preparation of carbon system

The active carbon (AC) was impregnated with ammoni-acal solutions of Cu(II) ethylenediamine (10% w/w) and Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate (10% w/w) for preparation of CuEDA/C and Cu6FAA/C systems respec-tively. Active carbon was impregnated with aqueous solution of 4.0% of NaOH for NaOH/C system. Modified Whetlerite (MWh) was prepared using two stages impregnation process. First stage included the impregnation of active carbon with ammoniacal solution of 6.0% copper (II) & 0.2% of silver (I) followed by initial drying at 110 °C and finally at 180 °C for complete removal of ammonia and for the second stage dried carbon system was further impregnated with aqueous
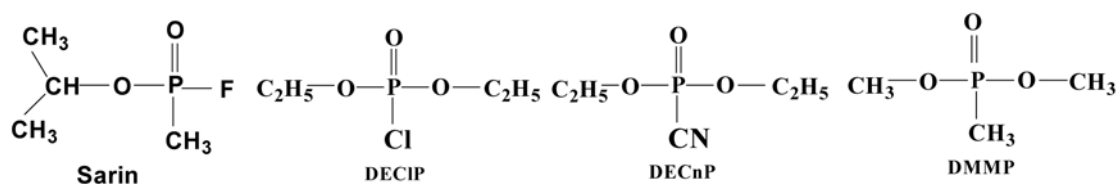
solution of 2.0% NaOH, 2.5% Cr(VI) and 2.5% pyridine followed by drying at 120 °C. The technique used for impregnation was incipient wetness technique [5-7]. Modified whetlerite was further impregnated with 2.0% NaOH for MWh/NaOH system. All impregnated carbons were dried at 110° C for 6 hrs, cooled in desiccator and finally kept in airtight containers till use.

2.3. Characterization

All carbon systems were extracted with water for the quantitative determination of metal ions such as copper & chromium using iodometric titrations and silver by atomic absorption spectrometer [28]. Percentage of extracted metal ions were found to be in close agreement with its theoretical values. BET surface area and micropore volume (HK method) of these carbons by nitrogen up take at liquid nitrogen temperature were determined on Autosorb 1C from Quantachrome (USA) and tabulated in Table 1. Fig. 1 represents the nitrogen adsorption isotherms of prepared systems.

2.4. Kinetic Experiments

In order to study the kinetics of degradation of simulants of nerve agents and sarin, 10 μl toxicant was mixed with 25 μl chloroform and spiked over 50 mg of carbon system in a stoppered glass tube. Multiple glass tubes were put to use for analysis at room temperature (25 ± 1 °C). After definite time intervals exposed carbons were extracted with 2.0 ml of chloroform and then extracts were analyzed for their residual amount of toxicant using gas chromatograph. Analysis was done at isothermal conditions, i.e., 90 °C column temperature using GC-8610 with BP-5 column and Flame ionization detector. The degradation of the agent over carbon systems was found to be following pseudo first order reaction kinetics as plots of Ln (a-x) verses time t were linear.

2.5. NMR

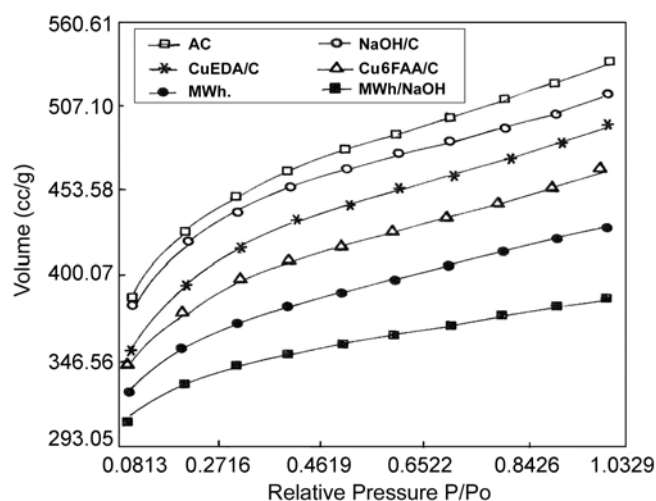To investigate into the degradation products, toxicant

Fig. 1. Nitrogen adsorption isotherm of carbon systems.

exposed MWh/NaOH system was extracted with methanol followed by purging with nitrogen gas to concentrate the extracted reaction products. NMR spectras of the concentrated extract were recorded in dimethylsulphoxide on Bruker 400 MHz NMR spectrometer.

3. Results and Discussion

Active carbon of surface area 1337 m^2/g was used for impregnation to obtaine modified whetlerite containing 2.0 or 4.0% NaOH. After impregnation surface area and micropore volume reduced to 1085 m^2/g and 0.53 cc/g respectively (Table 1). The reduction in the surface area and micropore volume is because of impregnants, which during impregnation travel through the macro pores and get deposited in the meso pores to cause the blocking of the meso/micro pores. Further impregnation of modified whetlerite carbon with additional 2.0% NaOH reduced surface area and pore volume to 1004 m^2/g and 0.50 cc/g respectively. Impregnation of active carbon with 10.0% Cu(II) ethylene diamine or 10.0% Cu(II) 1,1,1,5,5,5-hexa-fluoro acetylacetonate also resulted in the reduction of the

Table 1. Surface Area and Micropore Volume of carbon systems.

| S. No.	Carbon systems	Details of Impregnation	Surface area (m^2/g)	Micropore volume (cc/g)
1.	(MWh)	Whetlerite containing 2.0% NaOH	1085	0.53
2.	(MWh/NaOH)	Whetlerite containing 2.0% NaOH Plus additional 2.0% NaOH	1004	0.50
3.	(CuEDA/C)	Active carbon Plus 10.0% Cu(II) ethylenediamine	1246	0.58
4.	(Cu6FAA/C)	Active carbon Plus 10.0% Cu(II) 1,1,1,5,5,5-hexafluoro acetylacetonate	1167	0.56
5.	(AC)	Active carbon	1337	0.63
6.	(NaOH/C)	Active carbon Plus 4.0% NaOH	1307	0.62
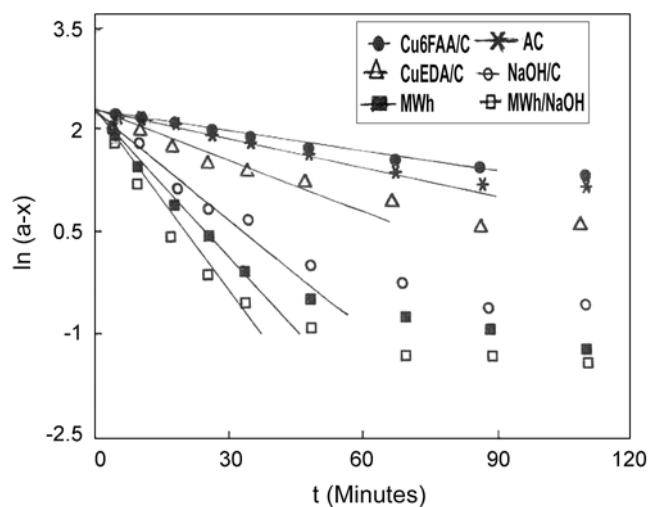
Fig. 2. Kinetics of degradation of DECIP.

surface area and micro pore volume (Table 1).

3.1. Kinetics of degradation of diethyl chlorophosphate, diethylcyanophosphonate and dimethyl methylphosphonate

Fig. 2 describes the plots of Ln of residual toxicants on Y-axis against reaction time t on X-axis. Linearity of curves shows the kinetics to be pseudo first order. Rate constant (K) was calculated using the slope of the straight line and half life ($t_{1/2}$) by 0.693/K and these are summarized in Table 2. The K values are the average of three runs with reproducibility within ± 5%. Initially the degradation of DEClP was found to be very fast which gradually slowed down to a steady state. Most probably it was due to the formation of reaction products, which are co-adsorbed on the carbon surface and works as a barrier for the reaction of DEClP with impregnants on basic surface of carbon. As nerve agents are more prone to hydrolysis, DEClP on hydrolysis produced acid of DEClP, which poisoned the basic nature of carbon surface. When active carbon was used for the degradation of DEClP half life and rate constant were found to be 50.9 minutes and 1.36×10^{-2} minutes^{-1} respectively. For active carbon impregnated with 4.0% NaOH, half life

drastically came down to 13 minutes and rate constant increased to 5.3×10^{-2} minutes^{-1}. It showed that the degradation of DEClP has increased due to the presence of NaOH.

As per literature ASC whetlerite [2] (without sodium hydroxide), which physisorbs nerve agents (no chemical degradation is reported) is impregnated with triethylene-diamine for providing stability to Cr(VI). But modified whetlerite used in indigenous NBC filtration systems contains 2.0% sodium hydroxide and 2.5% of pyridine for the stabilization of Cr(VI), in this way not only Cr(VI) is stabilized but it also provides much basicity to the carbon system and probably can provide favorable conditions for the degradation of CW agents. The degradation of DEClP over modified whetlerite containing 2.0% sodium hydroxide is found to be very fast with half life of 9.1 minutes. Probably it is due to the presence of sodium hydroxide, which was further confirmed with faster degradation capability shown by whetlerite containing 2.0% sodium hydroxide impregnated with additional 2.0% sodium hydroxide (MWh/NaOH system). This system degraded DEClP with half life of 7.9 minutes indicating further enhanced degradation. MWh/NaOH system degraded diethyl chlorophosphate to diethyl phosphate (DEP) (Scheme 1), which was confirmed by phosphorus (P^{31}) and proton (H^1) NMR spectras of reaction products. P^{31} NMR spectra of DEClP in dimethyl-sulphoxide (DMSO) showed peak at -1.624 ppm, which disappeared after degradation and new peak arose at 0.0298 ppm. New peak was due to diethyl phosphate, which was further confirmed by proton NMR spectra of degraded products in DMSO (Table 3), these NMR peak values were found to be in close agreement with existing libraries of these compounds.

Copper complexes are well known for catalyzing the hydrolysis of nerve agents (20). To investigate this on the surface of carbon, active carbon was impregnated with 10% w/w of Cu(II) ethylenediamine and Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate. Cu(II) ethylenediamine system CuEDA/C showed promising results over active carbon with half life of 27 minutes and rate constant 2.56×10^{-2} minutes^{-1}. However, Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate impregnated system Cu6FAA/C showed slow degradation of

Table 2. Kinetic parameters for degradation of DEClP, DECnP & Sarin.

S. No.	Carbon System	DEClP		DECnP		Sarin	
		$t_{1/2}$ (min)	K (min^{-1})	$t_{1/2}$ (min)	K (min^{-1})	$t_{1/2}$ (min)	K (min^{-1})
1.	(MWh)	9.1	7.67×10^{-2}	2.3	3.01×10^{-1}	39	1.77×10^{-2}
2.	(MWh/NaOH)	7.9	8.75×10^{-2}	1.5	4.62×10^{-1}	20	3.46×10^{-2}
3.	(NaOH/C)	13.0	5.30×10^{-2}	3.3	2.10×10^{-1}	97	0.71×10^{-2}
4.	(CuEDA/C)	27.0	2.56×10^{-2}	4.8	1.44×10^{-1}	866	0.08×10^{-2}
5.	(Cu6FAA/C)	68.6	1.01×10^{-2}	7.2	0.96×10^{-1}	1732	0.04×10^{-2}
6.	(AC)	50.9	1.36×10^{-2}	6.2	1.12×10^{-1}	1155	0.06×10^{-2}
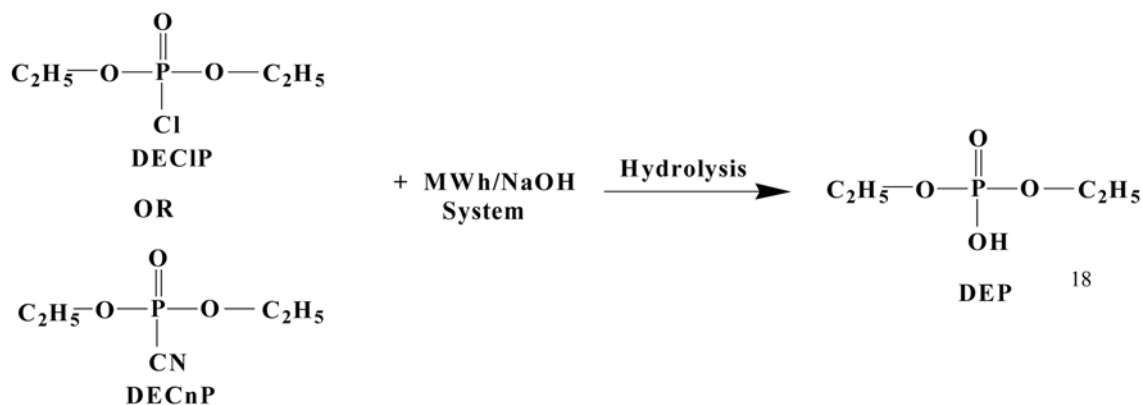
Scheme 1

Table 3. NMR data of toxicants and their degraded products.

NMR	DEClP (ppm)	DECnP (ppm)	Sarin (ppm)	DEP (ppm)	IMPA (ppm)
P^{31}	-1.624	-21.54	26.84, 33.24	0.0298	30.61
H^1	1.18 (CH_3), 3.89 (CH_2)	1.35 (CH_3), 4.3 (CH_2)	1.3 {(CH_3)$_2$}, 1.65 (PCH_3), 4.72 (CH)	1.21 (CH_3), 3.98 (CH_2)	1.39 {(CH_3)$_2$}, 1.22 (PCH_3), 4.51 (CH)

DEClP with half life of 68.6 minutes. Higher activity of CuEDA/C system in comparision to Cu6FAA/C system is due to more electropositive character of copper atom of Cu(II) ethylenediamine than the copper atom of Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate. The presence of less bulkier ligand on copper of Cu(II) ethylenediamine also facilitated the degradation of DEClP. Cu6FAA/C system showed least effectiveness for the degradation of DEClP amongst all systems. However, the degradation is even less than active carbon. It is probably due to the decrease in surface area and active sites of carbon system.

In order to confirm the less effectiveness of Cu6FAA/C system, active carbon was impregnated with 10% w/w of Cu(II) 1,1,1-trifluoroacetylacetonate and Cu(II) acetylacetonate for preparation of Cu3FAA/C and CuAA/C system respectively. All three systems, i.e., Cu6FAA/C, Cu3FAA/C and CuAA/C along with active carbon (AC) were exposed to DEClP. Order of reactivity was found to be CuAA/C > AC > Cu3F AA/C > Cu6FAA/C. Active carbon itself degraded DEClP in comparable amount due to its basic nature. The degradation shown by Cu6FAA/C system is due to active carbon only not because of impregnant as Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate alone (without carbon) did not show significant degradation of DEClP in solution phase reaction. It showed that these copper complexes of acetylacetonate do not facilitate the degradation of DEClP, however, CuAA/C degraded more DEClP than active carbon.

Fig. 3, the plot of Ln (a-x) against time t depicts the kinetics of degradation of diethyl cyanophosphate over prepared carbon systems and the order of reactivity was
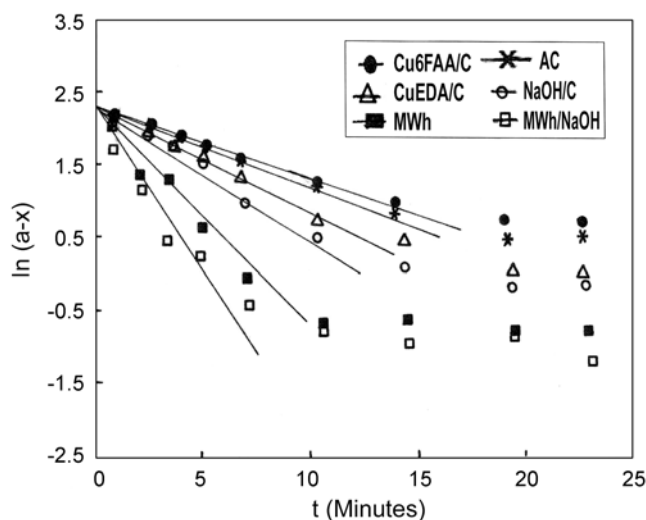

Fig. 3. Kinetics of degradation of DECnP.

found to be MWh/NaOH > MWh > NaOH/C > CuEDA/C > AC > Cu6FAA/C. Initially the degradation was very fast which slowed down as the degradation proceeded. It is due to the coadsorption of the reaction products causing surface poisoning of the carbon system. Half life and rate constant for the degradation of DECnP with MWh/NaOH system were found to be 1.5 minutes and 4.62×10^{-1} minute^{-1} respectively (Table 2). No detectable amount of DECnP was noticed after 30 minutes with MWh and MWh/NaOH systems. Cu6FAA/C system showed least degradation because
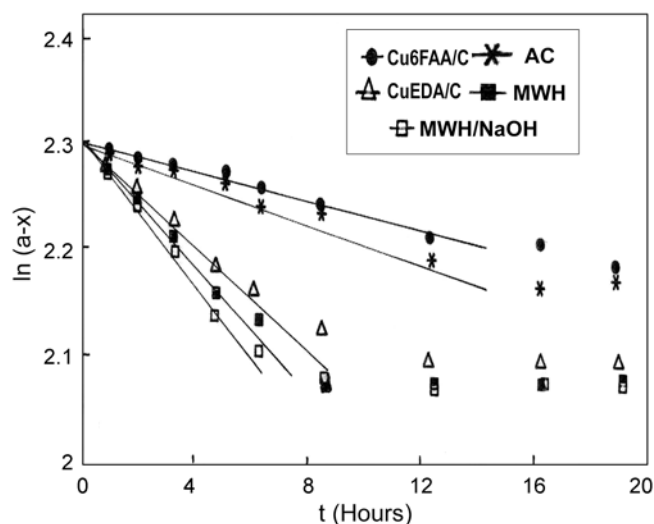
Fig. 4. Kinetics of degradation of DMMP.

Fig. 5. Kinetics of degradation of Sarin.

of inactiveness of the impregnant towards the reaction with DECnP. Phosphorus and Proton NMR spectras of DECnP and reaction products extract in dimethyl sulphoxide were recorded (Table 3). NMR spectras suggested the degradation product of diethyl cyanophosphate to be diethylphosphate (Scheme 1).

Kinetics of degradation for DMMP has been shown in Fig. 4. Degradation profile of DMMP for all prepared carbon systems was found to be same as of DEClP and DECnP. One major difference came across was the half life time for degradation. As in DEClP or DECnP the half life time was in few minutes but in case of DMMP half life time was found to be in hours. The reason behind this is the unavailability of reactive group associated with the phosphorus atom of DMMP, however, other simulants were reactive due to the presence of reactive groups such as chloro and cyano on the phosphorus atom of DEClP and DECnP respectively.

MWh/NaOH system was found to be showing the fastest degradation amongst all the systems. Fig. 4 shows that initially curves followed the straight line but afterwards deviated from straight line. The slope of straight line provided the rate constant (K), 3.45×10^{-2} hours^{-1} and half life (0.693/K), 20.1 hours for MWh/NaOH system, however, all the systems including MWh/NaOH could not show more
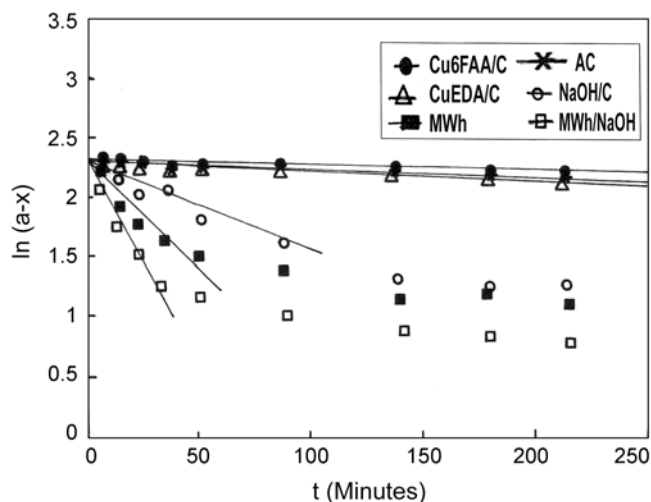
than 20% degradation of DMMP in 50 hours.

3.2. Kinetics of degradation of Sarin

Prepared carbon based adsorbent materials showed promising degradation capabilities against nerve agent simulants, which attracted our attention to check their potential against sarin, a nerve agent. Same experimental conditions were applied for the degradation of sarin and the kinetics of degradation was monitored with GC/FID. Rate constant and half life values were calculated using the straight lines of Fig. 5.

MWh, MWh/NaOH and NaOH/C systems could provide comparable degradation of sarin while the rest of three systems, i.e., AC, CuEDA/C and Cu6FAA/C showed slow reaction with sarin and seemed to be non-promising. MWh/NaOH system depicted maximum degradation efficiency amongst all the prepared systems. This system showed 50.0% degradation of sarin in 20.0 minutes with rate constant to be 3.46×10^{-2} minutes^{-1} (Table 2). NMR spectra of the reaction products showed that MWh/NaOH system degraded sarin into isopropylmethylphosphonic acid (IMPA) (Scheme 2). P^{31} NMR spectra of pure sarin gave peaks at 26.84 and 33.24 ppm. These peaks disappeared in the P^{31} NMR spectra of the extract of reaction product of sarin, while a new peak arose at 30.61 ppm, which is due to the
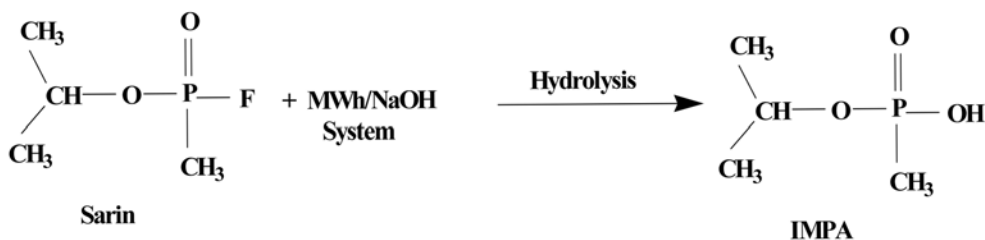
Scheme 2

formation of IMPA. Formation of IMPA was further confirmed by proton NMR spectra of degradation products (Table 3).

Copper complexes [21, 23] are well known for the degradation of sarin. This behavior was not found in CuEDA/C and Cu6FAA/C systems. CuEDA/C system showed half life of 866.2 minutes which is lower than the half life shown by active carbon alone (1155 minutes), however Cu6FAA/C system showed less degradation capability (half life, 1732.5 minutes) than active carbon. It is due to the inactiveness of Cu(II) 1,1,1,5,5,5-hexafluoroacetyl-acetonate against sarin because it does not have highly positive copper atom and is sterically hindered which is the basic requirement of a copper complex to be reactive [20]. Cu(II) ethylenediamine fulfills these requirements and showed higher degradation of sarin than active carbon. Promising results shown by MWh, MWh/NaOH and NaOH/C systems are due to the presence of sodium hydroxide, which facilitates the degradation of sarin. Both the whetlerite systems (MWh and MWh/NaOH) showed lesser $t_{1/2}$ values than NaOH/C system indicating that not only sodium hydroxide but other impregnants of whetlerite also play an important role for the degradation of sarin, which is to be further explored.

Modified whetlerite adsorbent material, which is currently in use with Indigenous NBC filtration systems is capable of degrading inorganic gases such as cyanogens chloride, hydrogen chloride and phosgene [29]. The present study depicted that indigenous modified whetlerite (with NaOH) can also degrade nerve agents efficiently, while conventional whetlerite [2] (without NaOH) does not degrade nerve agents but merely holds them by physical adsorption. Interesting results for the degradation of nerve agents brought our attention to check its potentiality against other type of persistent CW agents i.e., blister agent (sulphur mustard). Promising results were obtained and shall be reported else where after completion of study. However, 100 mg of MWh/NaOH system exposed to 5 μl of sulphur mustard showed 70% degradation in 72 hrs.

4. Conclusion

Carbon based adsorbent materials such as MWh, MWh/NaOH and NaOH/C were found to be promising adsorbents for in-situ degradation of nerve agent simulants such as DEClP, DECnP, DMMP and sarin, an actual CW agent. Most probably, it is due to the presence of sodium hydroxide. MWh/NaOH adsorbent system provided maximum degradation of all studied organophosphorus compounds and it was even better than NaOH/C system. It revealed that not only sodium hydroxide but other impregnants of whetlerite also played an important role in degradation, which is to be further explored. 50 mg of Wh/NaOH system could

neutralize 5.0 μl of sarin out of 10 μl in 20 minutes. Reaction products with MWh/NaOH system were found to be the corresponding acids of used toxicants. Cu(II) 1,1,1,5,5,5-hexafluoroacetylacetonate showed least degradation potential which was even less than active carbon and can not be used for nerve agents degradation, however, Cu(II) ethylenediamine has some potential. Present study revealed that modified whetlerite containing 2.0% sodium hydroxide has a potential against both type of persistent chemical warfare agents such as nerve and blister agents. Additional 2.0% sodium hydroxide could further enhance its efficiency. Finally, it can be concluded that modified whetlerite adsorbent system containing 2% NaOH or more not only degrades non-persistent CW agents but can also degrade persistent CW agents. Therefore, it can provide protection against the wide spectrum of CW agents and can probably be incorporated in NBC filtration systems as an effective adsorbent material.

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