

Adsorption of 1,1-Dimethylhydrazine by Hydrolysis Lignin

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ABSTRACT: *Many modern launch vehicles use unsymmetrical dimethylhydrazine (UDMH) as liquid fuel in the space program. UDMH is highly toxic and poses a serious threat to the environment and to humans. One of the most effective methods of UDMH neutralization in case of fuel spills is adsorption. This paper is the first to suggest using hydrolysis lignin as rocket fuel adsorbent. The research was based on the use of ion chromatography with amperometric detection and gas chromatography-mass spectrometry methods. The adsorption experiment resulted in finding the conditions that correspond to the residual UDMH concentration that does not exceed maximum permissible concentration in water. Also, it was investigated the effect of moisture content of hydrolysis lignin and ambient temperature on the dynamics of UDMH adsorption from the gaseous phase. We determined the kinetic and thermodynamic parameters of the adsorption process. It was demonstrated that the reaction between 1,1-dimethylhydrazine and active adsorbent centers (carbonyl and carboxyl groups) is close to the first order. The value of activation energy (85.9 kJ/mol) corresponds to that of chemisorption.*

KEYWORDS: *Adsorption; 1,1-dimethylhydrazine; Lignin; Rocket fuel; UDMH.*

INTRODUCTION

Unsymmetrical dimethylhydrazine (UDMH) is one of the components in rocket fuel and is used to propel rockets produced by many countries, e.g. Indian (PSLV), Russian (Proton, Tsyklon, Kosmos), USA (Titan), French (Ariane), Japanese (N-family rockets), and Chinese (Great March) launch vehicles [1-3].

Environmental contamination by Rocket Fuel Components (RFC) based on UDMH and its derivatives [4, 5] is a major environmental concern due to their high toxicity (Table 1) and volatility [6]. UDMH has also been proven to have oncogenic and mutagenic properties [8, 9]. In the course of aerospace activities on the launch sites

and in fueling areas, there is a risk of spills of high-toxicity rocket fuel containing UDMH that poses a significant risk of pollution to the air and water environment. A response to such pollutions is a very convoluted task that requires huge financial expenditure. Due to its high volatility, one of the main routes of UDMH entry into the human body is inhalation. Upon entry of UDMH into the environment, it is mandatory to take prompt and immediate measures towards its containment and cleanup [10, 11].

One of the primary means of UDMH inactivation is the use of rocket fuel adsorbents able to bind hydrazines into inactive forms for subsequent high temperature disposal.

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Table 1: Maximum permissible concentration (MPC) of UDMH in the environment.

Object	MPC	Organization, country
Water	0.02 mg/L	Russian Federation
Soil	0.1 mg/kg	Russian Federation
	0.05 mg/kg	Kazakhstan
Air	0.1 mg/m ³ (launch site)	Russian Federation
	0.001 mg/m ³ (ambient)	Russian Federation
	1.25 mg/m ³	Occupational Safety and Health Administration (OSHA), USA
	0.15 mg/m ³ (120 min exposition)	National Institute for Occupational Safety and Health (NIOSH), USA
	1.25 mg/m ³	American Conference of Industrial Hygienists (ACGIH), USA

A previously published paper [12] presents an analysis of currently available technologies intended for inactivation of fuel-contaminated soils. Presently there are several adsorbents that demonstrate high affinity to UDMH. Among them are: adsorbents based on activated charcoal, natural and sulfuric peat; adsorbents based on peat and charcoal treated with superheated steam; adsorbents based on modified highbog peat that contain salts of transition metals; and a shungite-based adsorbent modified with manganese and ferrous oxides. Another known method of air purification from UDMH is based on the use of a ligand-exchange adsorbent with high affinity to ammonia and amines [13]. A common shortcoming of the aforementioned adsorbents is their high cost and complex multistage production.

As a result, the development of new adsorbents that comply with the following requirements remains a pressing concern: availability, low cost, simple production and efficiency, i.e. high UDMH adsorption from gaseous and liquid media, thus bringing UDMH concentration down to allowable levels.

The sources present data on the behavior of toxic components of the rocket fuel and its transformation products in various media, including various kinds of soils [14-22]. Previously we have investigated the adsorption performance of peat with respect to UDMH [23, 24] where we had determined the prevailing role of lignin and humic substances contained in boggy soil in chemical transformations of UDMH. It was shown that lignin is marked by pronounced retention of UDMH derivatives, as compared to peat and humic acids. Based on the chemical properties of hydrazines [25] and peat functional composition it is evident that the main

functional groups of lignin-humic substances being able to bind UDMH are carbonyl groups that react with UDMH through nucleophilic bonding mechanism, thus producing hydrazones. Carboxyl groups react via a salification mechanism. Also, it is possible the reaction between UDMH and carbon-carbon double bonds, which is similar to the reaction between hydrazines and alkenes.

In view of the above, the adsorbents based on lignin containing materials [26] are of special interest to the development of methods for neutralization of UDMH spills. Hydrolysis lignin is a cheap and available high-yield byproduct of bioethanol production is considered as one of the most promising sources of such adsorbents [27].

In this connection, the purpose of this paper is to research the interactions between hydrolysis lignin and 1,1-dimethylhydrazine, and to evaluate its application as adsorbent of 1,1-dimethylhydrazine to purify aqueous and gaseous media.

EXPERIMENTAL SECTION

Materials and reagents

The main criterion in choosing the test object for further development of UDMH adsorbent was finding a source of available lignin-humic compounds. Hydrolysis lignin (HL) was chosen as the source. HL is a complex industrial product that comprises about 70% of lignin and humic compounds that have formed in the course of long-term storage in stockpiles. Specifications of the test object are given in Table 2. To obtain the HL preparations with different moisture contents absolutely dry sample (dried in an oven at 105°C to constant weight) was mixed with an appropriate amount of water in an airtight container and equilibrated overnight.

Table 2: Specifications of HL used as UDMH adsorbent.

Moisture content, %	Ash content, %	Components, %		Functional groups, %				
		Humic compounds	Klason lignin	COOH	OH	COOH+OH	CO	OCH ₃
5.1±0.1	2.6±0.3	7.2±0.4	69.8±2.5	1.73±0.09	3.02±0.10	4.75±0.12	3.37±0.40	20.06±0.39

1,1-dimethylhydrazine (Fluka) containing at least 97% of the base material was used in the course of the research.

Safety warning: UDMH is extremely toxic and flammable compound. Avoid contact with skin and eyes. Avoid inhalation of vapour or mist. Use explosion-proof equipment. Keep away from sources of ignition. Any scale-up of procedures described in the manuscript would require diligent caution.

Investigation of adsorption in aqueous media

Analysis of UDMH adsorption by hydrolysis lignin was conducted in static conditions at optimum pH value (5.5), which was determined in the course of UDMH adsorption using highbog peat, a value that corresponds to the maximum UDMH adsorption performance of lignin-humic compounds [23]. The research was carried out at a steady temperature of 25 °C and the following variables: UDMH concentration 20–500 mg/L; adsorption time 1–24 h at UDMH concentration of 20 mg/L. All experiments were performed in three replicates.

Lignin samples were placed into 100 mL cone-shaped test jars sealed with plugs. Required acidity levels of the medium were ensured using a universal buffer solution. In order to guarantee proper soaking of the adsorbent, each lignin sample was immersed into 25 mL of the buffer solution and exposed for 24 h with occasional stirring. Then 25 mL of UDMH of a predetermined concentration was added (UDMH was diluted in universal buffer solution) and held at 25 °C for a specified time with continuous stirring. Upon expiry of the adsorption time, the solution was filtered through a nylon membrane filter, pore diameter 0.2 µm. After that, the UDMH equilibrium concentration in the filtrate was determined using ion chromatography and amperometric detection methods [28, 29].

In the course of the research, we employed an HPLC Stayer (Akvilon, Russia) system consisting of isocratic pump, column oven, manual injector, and amperometric

detector. The hydrazines were separated in the cationic form using a separation column loaded with the sulfonation-exchange stationary phase (Nucleosil 100–5 SA, Macherey Nagel, Germany). Acetate buffer solution pH 5.4 was used as eluent. The measurements were conducted at an eluent flow rate of 1 mL min⁻¹. The potential of the glass-carbon electrode was +1.3V.

Experimentally obtained results were quoted in the form of UDMH recovery value expressed as a percentage of the initial content, as well as residual UDMH concentration in the solution and UDMH adsorption factor in mg/g determined as:

$$C_a = \frac{(C_i - C_e)V}{g} \quad (1)$$

Where C_a is the amount of adsorbed UDMH, mg/g; C_i and C_e are the initial and equilibrium UDMH concentrations in the solution, mg/L; V is the volume of the solution, L; and g is the weight of the air-dried adsorbent, g.

Investigation of adsorption in the gaseous phase

Analysis of the efficiency of hydrolysis lignin in the purification of gaseous media by removal of 1,1-dimethylhydrazine was conducted by introducing the adsorbent and concentrated 1,1-dimethylhydrazine into air-tight vials and determining the UDMH concentration in the vapor phase above the adsorbent at predetermined time intervals. The adsorbent was placed inside a 20 mL vial and UDMH was introduced into a smaller 2 mL vial inside the bigger vial using a syringe, to prevent contact between the contaminant and adsorbent. The experiment was conducted at UDMH-to-adsorbent ratio of 12 mg to 1 g at 24–35 °C. The exposure time was 10 to 450 min and adsorbent moisture content was 30%.

The analysis of how the moisture contained within hydrolysis, lignin affects the adsorption of 1,1-dimethylhydrazine was conducted by introducing the adsorbent and concentrated 1,1-dimethylhydrazine

into air-tight vials (in this case, the liquid phase of UDMH was in contact with the solid phase of the adsorbent) and determining the UDMH concentration in the vapor phase above the adsorbent at predetermined time intervals at 30 °C, and levels of moisture content in the adsorbent between 5 and 80%, and adsorption times ranging from 10 to 450 min. To ultimately rule out the influence of UDMH oxidation on the adsorption, the experiments were conducted in a helium atmosphere.

Gas samples were taken from time to time and analyzed for the presence of UDMH using GC-MS. Experimental results were expressed as the concentration of unconjugated gaseous UDMH in mg m^{-3} . The samples were analyzed by gas chromatograph-mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Japan), equipped with autosampler AOC 5000 and headspace injection system. Chromatographic separation was by quartz capillary column Rtx-5ms (Restek, USA), diameter 0.25 mm, length 30 m, stationary phase 0.25 μm . The sample volume was 250 μl with flow split of 1:100, and injector temperature 230 °C. The separation was conducted at a constant temperature of 40 °C for 2 min (isotherm 2 min.). Carrier gas flow (hydrogen, 99.9999 %) in the column was maintained at 1.2 ml min^{-1} at a constant pressure of 9.5 kPa. Mass spectrometric detection was accomplished using the following detector parameters: ionization mode, electron impact; ionization energy 70 eV; detector voltage 0.7 kV; temperature of mass spectrometer interface 230 °C; ion source temperature 230 °C; and mass detector operation mode, Selected Ion Monitoring (SIM). Measured ions, m/z : 42, 45 and 60.

Absolute values of the UDMH concentration were determined using calibration dependence between area response and concentration of 1,1-dimethylhydrazine in the gaseous phase, which is described by the following linear equation:

$S = 7.059C_{\text{UDMH}}$ (range of concentrations 50–2000 mg m^{-3} , $R^2 = 0.9955$).

Gaseous samples with known UDMH concentrations were prepared by introducing a methanol-based solution of UDMH into vials whereby the volatile solvent evaporated together with the solute and all UDMH was in gaseous form.

To increase sensitivity when measuring lower UDMH concentrations, the final stages of the experiment were conducted at a split ratio of 1:5. The detector

voltage was set to 0.86 kV, other parameters of flow split and detection were similar to those indicated above. The calibration dependence between area response and concentration of 1,1-dimethylhydrazine in the gaseous phase in these conditions is described by the following linear equation:

$S = 263.92C_{\text{UDMH}}$ (range of concentrations 0.2–600 mg/m^3 , $R_2 = 0.9991$).

RESULTS AND DISCUSSION

UDMH adsorption from solution

In the course of the research, we studied the effect of UDMH concentration and the duration of contact between the phases on the process of adsorption by hydrolysis lignin.

The dependence between UDMH recovery and the adsorbate/adsorbent ratio is shown in Fig. 1. The dependence between the volume of the solution and the mass of the adsorbent (V/m) was chosen to correspond to the maximum recovery value established by preliminary experiments.

As a result, it was established that the maximum UDMH recovery is observed when UDMH concentration was 20 mg/L (0.5 mg of UDMH per 1 g of lignin). In this case, it amounted to 97.5% of the initial UDMH content in the solution. The residual UDMH concentration was 0.5 mg/L and exceeded MPC in water (0.02 mg/L) by 25 times.

In view of this, we investigated UDMH adsorption dynamics using hydrolysis lignin when UDMH concentration in the solution was 20 mg/L for periods of 1 to 24 h (Table 3).

Therefore, we established that when adsorption time was 24 h, the ratio of solution to adsorbent was 25:1, and UDMH concentration was 0.5 mg/g of the adsorbent (20 mg/L), the UDMH concentration in the solution (0.016 mg/L) did not exceed MPC (0.02 mg/L) and corresponded to a UDMH recovery of 99.92%.

UDMH adsorption from a gaseous medium

Since hydrolysis lignin has a relatively high affinity to UDMH when adsorbing it from a solution, the conjecture was made that the adsorbent could also be used to prevent air contamination with vaporized 1,1-dimethylhydrazine which occurs in the event of a UDMH spill.

One of the primary factors that define the efficacy of adsorption is the amount of moisture in the adsorbent,

Table 3: UDMH adsorption dynamics using hydrolysis lignin at the UDMH concentration of 20 mg/L. $C_{UDMG} = 20$ mg/L; $V/m = 25/1$; pH 5.5; $T = 25^\circ\text{C}$.

Time, h	Residual UDMH concentration, mg/L	UDMH recovery, %
0	20 ± 2	0
1	7.0 ± 0.8	65 ± 4
2	1.8 ± 0.2	91 ± 1
3	0.80 ± 0.09	96.0 ± 0.4
4	0.50 ± 0.06	97.5 ± 0.3
5	0.47 ± 0.06	97.7 ± 0.3
24	0.016 ± 0.002	99.92 ± 0.01

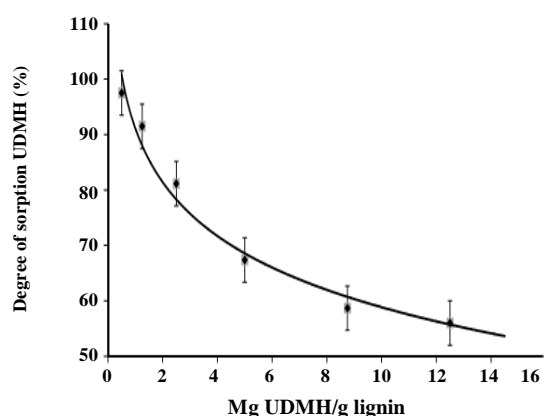


Fig. 1: Dependence between recovery and UDMH concentration. Adsorption time – 2 hours, $V/m = 25/1$, pH 5.5, $T = 25^\circ\text{C}$.

which may influence the processes of physical and chemical adsorption. In the presence of water, the adsorbent increases its volume and thus increases its specific surface area. It also leads to an enhanced rate of diffusion of the adsorbed substance onto the adsorbent surface. The increased concentration of hydrogen ions in the system may influence the rate of chemical interaction between UDMH and active adsorbent centers.

In view of this, we investigated the adsorption dynamics of 1,1-dimethylhydrazine using hydrolysis lignin in air-dried and wet form, and also determined the UDMH concentration in the vapor phase over the adsorbent by using GC-MS (Fig. 2) [22]. This experiment was considered as a simulation of a real rocket fuel spill and its adsorption using hydrolysis lignin. It also allowed determination of the content of 1,1-dimethylhydrazine in the gas phase over the adsorbent, since in case of spills of UDMH-based rocket fuel its physical properties entail air contamination.

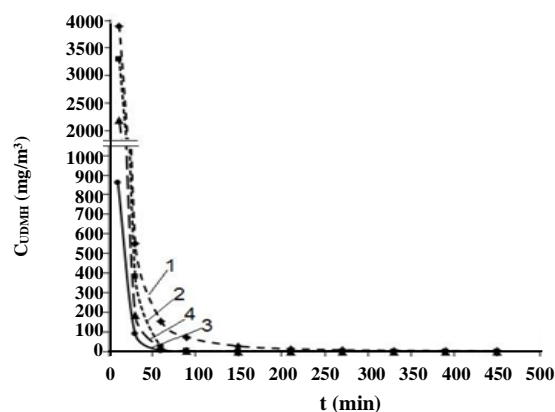


Fig. 2: UDMH adsorption dynamics using hydrolysis lignin having the following moisture content values: 1 – 5 %; 2 – 30 %; 3 – 50 %; 4 – 80 %; $T = 30^\circ\text{C}$.

In the course of the experiment, the moisture content varied from 5 to 80%. In this case, the physical form of the adsorbent ranged from a powder-like state (moisture content 5–30%) to a paste-like state (moisture content 30–80%).

It was found that the presence of any amount of moisture in the adsorbent initially results in a pronounced decrease of UDMH concentration in the gaseous phase over the adsorbent. With adsorption times over 1 h the rate of adsorption decreases rapidly.

To analyze more accurately the results obtained in the course of the experiment, we determined the kinetic properties of the UDMH adsorption process (rate constant, the order of reaction) with variable moisture levels in the adsorbent (Table 4). In order to determine the kinetic properties we developed linear dependencies $\ln(-dc/dt) = n \cdot \ln c + \ln k$ (Fig. 3) and obtained the equation parameters that allowed determination of rate constant (k) and individual orders of reaction that 1,1-dimethylhydrazine enters into (n).

Table 4: Rate constants (k) and orders of reaction (n) of the UDMH adsorption using hydrolysis lignin having 5–80 % of moisture content.

The moisture content of the adsorbent, %	n	k
5	1.51	0.0023
30	1.09	0.067
50	0.99	0.12
80	0.94	0.10

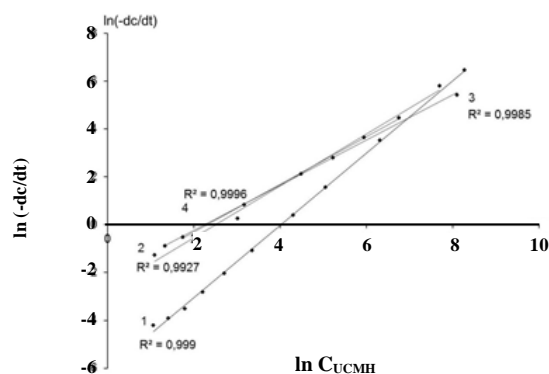


Fig. 3: Dependencies $\ln(-dc/dt)$ of $\ln c$ for the UDMH adsorption using hydrolysis lignin having the following moisture content values: 1 – 5 %; 2 – 30 %; 3 – 50 %; 4 – 80 %.

The results enabled us to conclude that increasing the moisture content in the adsorbent enhances the adsorption rate when the moisture is within 5 to 50%, while further increases in moisture levels up to 80% slightly diminish the adsorption rate. Noticeable increases in adsorption rate occur in the range of 5 to 30% (29 times); at the same time increasing the moisture content in the range of 30 to 80% yields little change. This effect is due to the interaction between UDMH and water, and further reaction between an aqueous solution of 1,1-dimethylhydrazine or corresponding protonated molecule and surface adsorption centers in the lignin macromolecules. Increasing the water content of the adsorbent also raises the concentration of hydrogen ions in the system, which in low concentrations catalyze the formation of hydrazones [25]. Reduced adsorption rate when the moisture content is 80% is probably driven by a higher degree of protonation of UDMH and increased the concentration of hydrogen ions, which reduces its reactivity.

In the case of air-dried hydrolysis lignin (moisture content 5%) the total rate of UDMH adsorption

is influenced both by diffusion and by chemical interaction processes; i.e. the process has multiple stages and occurs in a diffusion-kinetic area as evidenced by the fractional order of the reaction. In the presence of water, the total rate of adsorption is determined by the limiting stage of chemical interaction between UDMH and functional groups (the process occurs in the kinetic area) and in this case the reaction is close to first order (Table 4).

Notwithstanding some differences in adsorption rate at the initial stages of the process, the use of adsorbents with a moisture content of 30–80% leads to a reduction of the UDMH concentration in the gaseous phase below the detection level (Fig. 2). When moisture levels are over 30% the adsorbent is no longer a powder, which may interfere with its application. Therefore, from the standpoint of performance characteristics the efficacy of UDMH adsorption is optimal when the moisture content is about 30%.

After 10 min of application, the UDMH adsorption performance of hydrolysis lignin with a moisture content of 30% reaches 99.63%. The same parameter measured after 30 min amounts to 99.97%. In this case, the bulk of 1,1-dimethylhydrazine is bound to water molecules in the adsorbent immediately after being introduced. Later, UDMH is adsorbed by the active adsorption centers of lignin.

To understand fully the nature and mechanism of this behavior, it is necessary to determine the thermodynamic parameters of the process. In view of this, we investigated the UDMH adsorption dynamics using hydrolysis lignin at 24, 30 and 35 °C (Fig. 4).

The effect of temperature on the adsorption dynamics of 1,1-dimethylhydrazine by hydrolysis lignin was analyzed which allowed the determination of the kinetic and thermodynamic properties of the process (rate constant (k), the order of reaction (n), activation energy (E_a), and enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of activation), given in Table 5.

Table 5: Kinetic and thermodynamic properties of UDMH adsorption using hydrolysis lignin in the temperature range of 24 to 35 °C.

T, °C	n	k	E _a , kJ/mol	ΔH [‡] , kJ/mol	ΔS [‡] , J/molK
24	1.43	0.0012	85.9	84.3	-13.6
30	1.34	0.0036			
35	1.25	0.0094			

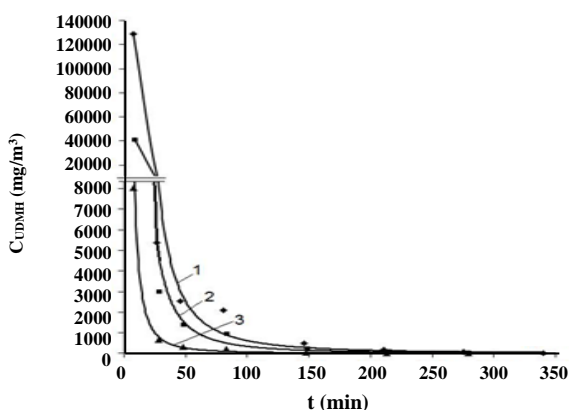


Fig. 4: UDMH adsorption dynamics using hydrolysis lignin at various temperatures: 1 – 24 °C, 2 – 30 °C, 3 – 35 °C.

In order to determine the kinetic properties, the dependencies shown in Fig. 4 were differentiated at various times. The data obtained were used to build linear dependencies $\ln(-dc/dt) = n \cdot \ln c + \ln k$ and to find the equation parameters that allowed establishing of the rate constant (k) and the individual orders of reaction that 1,1-dimethylhydrazine enters into (Table 5).

The results demonstrated that a 5 °C increase in temperature speeds up the adsorption process by 2.5–3 times. The fractional order of the reaction is evidence of a complex multistage process where the total UDMH adsorption rate is influenced both by diffusion and by chemical interaction with active adsorbent centers. It was noted that increased temperature lowers the order of the reaction. This is probably associated with how temperature affects the rate of chemical adsorption. Since increased temperature facilitates chemical adsorption, the higher the temperature, the more effect the chemical interaction has on the total rate of the process as compared with diffusion (order of the reaction is closer to 1).

The obtained values of adsorption rate constants at various temperatures were substituted into the Arrhenius equation to determine the activation energy. Activation

energy obtained using the formula $\ln k = f(1/T)$ ($R^2 = 0.998$) amounts to 85.9 kJ mol⁻¹ (Table 4).

According to the theory of absolute reaction rates, using the Eyring equation and employing the graphical method, we obtained the values of activation enthalpy and entropy (Table 5).

High values of the activation energy (E_a) and activation enthalpy (ΔH^\ddagger) bear witness to the process that proceeds through the formation of an activated complex. The value of activation energy corresponds to the range of activation energies for the majority of chemical reactions (50–200 kJ/mol) which testifies to the defining role of chemical interaction in the process of UDMH adsorption by hydrolysis lignin. Here, the chemisorption is probably attributed not to the fast reactions where hydrazine protonation occurs, but to much slower processes, ostensibly the reactions between 1,1-dimethylhydrazine and carbonyl compounds that result in the formation of Schiff bases. This rather small value of the activation entropy (ΔS^\ddagger) can be explained by a reduction in the number of particles in the system due to the UDMH extraction from the gaseous phase by active adsorbent centers.

The research of the adsorption dynamics of UDMH vapors by hydrolysis lignin resulted in the conclusion that after 10 min, the recovery at 24, 30 and 35 °C amounts to 93.9, 96.2 and 99.3%, respectively; and after 30 min, to 99.2, 99.5 and 99.9%, respectively.

CONCLUSIONS

1- It was concluded that hydrolysis lignin possesses considerable adsorption properties with respect to UDMH, which is associated with its high concentration of carbonyl and carboxyl groups.

2- Hydrolysis lignin actively binds UDMH in the aqueous and gaseous phase, so can be used to manufacture high-efficiency adsorbents for toxic rocket fuel.

3- The research demonstrated the efficacy of hydrolysis lignin for the purpose of adsorption of 1,1-dimethylhydrazine from solution. UDMH recovery from solution reaches 99.92% in 24 h.

4- The research demonstrated that moisture content in the adsorbent greatly influences the UDMH adsorption process. The optimum value of the moisture content of hydrolysis lignin is 30%.

5- In the course of research, we determined the values of activation energy (85.9 kJ mol^{-1}), activation enthalpy (84.3 kJ/mol) and entropy (-13.6 J/mol K) of UDMH adsorption by hydrolysis lignin. It was demonstrated that the order of reaction between 1,1-dimethylhydrazine and active sorbent centers is close to first order. The activation energy value corresponds to that of chemisorption.

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REFERENCES

- [1] Vasant G., Suresh B.N., [History of Rocketry in India](#), *Acta Astronautica*, **65**(11–12):1515–1519 (2009)
- [2] Blinov V.N., Ivanov N.N., "Rakety-nositeli. Proekty i Realnost. Book 1. Rakety-Nositeli Rossii i Ukrainy", OmGTU, Omsk, Russia (2011).
- [3] Blinov V.N., Ivanov N.N., "Rakety-nositeli. Proekty i Realnost. Book 2. Zarubezhnie Rakety-Nositeli", OmGTU, Omsk, Russia (2011).
- [4] Rodin I.A., Moskvina D.N., Smolenkov A.D., Shpigun O.A., [Transformations of Asymmetric Dimethylhydrazine in Soils](#), *Russian Journal of Physical Chemistry*, **82**(6): 911-915 (2008).
- [5] Rodin I.A., Smirnov R.S., Smolenkov A.D., Shpigun O.A., Krechetov P.P., [Transformations of Unsymmetrical Dimethylhydrazine in Soils](#), *Eurasian Soil Science*, **45**(4): 386–391 (2012).
- [6] Choudhary G., Hansen H., [Human Health Perspective on Environmental Exposure to Hydrazines: A Review](#), *Chemosphere*, **37**(5): 801–843 (1998).
- [7] Kushneva V.S., Gorshkova R.V., "Handbook on toxicology and hygienic standards for potentially hazardous compounds", Revised Version, Izdat, Moscow, Russia (1992).
- [8] Armour M. A., "Hazardous Laboratory Chemicals Disposal Guide", CRC Press Inc., Boca Raton, FL (1991).
- [9] Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. World Health Organization, International Agency for Research on Cancer. 1972-Present. (Multivolume Work). Geneva (1999).
- [10] American Conference of Governmental Industrial Hygienists. TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, Cincinnati, OH: ACGIH Worldwide (2000).
- [11] Cook L., Glemm R., [Evaluation of Atmospheric Concentrations of Hydrazine and Unsymmetrical Dimethylhydrazine in and Around the Rocky Mountain Arsenal Hydrazine Facility](#)", Industrial Hygiene Special Study, No. 35-0101-77, AD-A285 332/2GEN, Denver, CO (1977).
- [12] Zhubatov Zh.K., Naurizbaev M.K., Tovasarov A.D., Alexeeva D.S., Bisarieva Sh.S., Analysis of Methods and Technologies of Detoxification of Soils Polluted with Rocket Fuel Components (in Russian), Herald of the Kazakh National Institute of Technology, *Named After K. I. Satpaev*, **1**: 186-191 (2010).
- [13] Leikin Ju.A., Kirillov E.A., Sorbent Isolation and Separation of Ammonia and Its Derivatives and Method of its Ireparation, *RF Patent 2061542, 10.06.* (1996).
- [14] Kasimov N.S., Krechetov P.P., Koroleva T.V. [Experimental Studies of Rocket Fuel Behavior in Soils](#), *Doklady Earth Sciences*, **409**(5): 744–746 (2006).
- [15] Zaitsev A.S., Gongalsky K.B., Gorshkova I.A., Krechetov P.P., Koroleva T.V., [Impact of Rocket Propellant \(Unsymmetrical Dimethylhydrazine\) on Soil Fauna](#), *Doklady Earth Sciences*, **440**(1): 1340-1342 (2011).
- [16] Braun B.A., Zirrolli J.A., "Environmental Fate of Hydrazine Fuels in Aqueous and Soil Environments", Final Rep., Eng. and Services Lab., Tyndall Air Force Base., ESL-TR-82-45 (1983).

- [17] Smolenkov A.D., Krechetov P.P., Pirogov A.V., Koroleva T.V., Bendryshev A.A., Shpigun O.A., Martynova M.M., [Ion Chromatography as a Tool for the Investigation of Unsymmetrical Hydrazine Degradation in Soils](#), *International Journal of Environmental Analytical Chemistry*, **85**(14): 1089–1100 (2005).
- [18] Kenessov B., Alimzhanova M., Sailaukhanuly, Y., Baimatova, N., Abilev, M., Batyrbekova, S., Carlsen, L., Tulegenov, A., Nauryzbayev, M. [Transformation Products of 1,1-dimethylhydrazine and Their Distribution in Soils of Fall Places of Rocket Carriers in Central Kazakhstan](#), *Science of the Total Environment*, **427–428**: 78–85 (2012).
- [19] Kenessov B., Koziel J. Grotenhuis, T., Carlsen, L. [Screening of Transformation Products in Soils Contaminated with Unsymmetrical Dimethylhydrazine Using Headspace SPME and GC-MS](#), *Analytica Chimica Acta*, **674**: 32–39 (2010).
- [20] Ul'yanovskii N.V., Kosyakov D.S., Pikovskoi I.I., Khabarov Yu.G., [Characterisation of Oxidation Products of 1,1-dimethylhydrazine by High-Resolution Orbitrap Mass Spectrometry](#), *Chemosphere*, **174**: 66–75 (2017).
- [21] Kosyakov D.S., Ul'yanovskii N.V., Bogolitsyn K.G., Shpigun O.A. [Simultaneous Determination of 1,1-Dimethylhydrazine and Products of its Oxidative Transformations by Liquid Chromatography–Tandem Mass Spectrometry](#), *International Journal of Environmental Analytical Chemistry*, **94**: 1254–1263 (2014).
- [22] Kosyakov D.S., Ul'yanovskii N.V., Pokryshkin S.A., Lakhmanov D.E., Shpigun O.A. [Rapid Determination of 1,1-dimethylhydrazine Transformation Products in Soil by Accelerated Solvent Extraction Coupled with Gas Chromatography–Tandem Mass Spectrometry](#), *International Journal of Environmental Analytical Chemistry*, **95**: 1321–1337 (2015).
- [23] Semushina M.P., Bogolitsyn K.G., Kozhevnikov A.Yu., Kosyakov D.S., [Study of the Process of Unsymmetrical Dimethylhydrazine with Peat \[in Russian\]](#), *Ekologia i Iromishlennost Rossii*, **7**: 58–60 (2012).
- [24] Ul'yanovskii N.V., Pokryshkin S.A., Kosyakov D.S., Kozhevnikov A.Yu., Ivahnov A.D., Bogolitsyn K.G., [Chromato-Mass Spectrometric Identification of 1,1-Dimethylhydrazine Transformation Products in Peat Bog Soil \[in Russian\]](#), *Khimiia rastitel'nogo syr'ja (Chemistry of Plant Raw Material)*, **3**: 181–187 (2012).
- [25] Audrieth L.F., Ogg B.A., “The Chemistry of Hydrazine”, John Wiley & Sons, Inc., New York (1951).
- [26] Bouguettoucha A., Reffas A., Chebli D., Amrane A., [Adsorption of the Cationic Dye Ethyl Violet on Acid and Alkali-Treated Wild Carob Powder, A Low-Cost Adsorbent Derived from Forest Waste](#), *Iran. J. Chem. Chem. Eng. (IJCCCE)*, **36**(1): 87–96 (2017).
- [27] Rabinovich M.L., Fedoryak O., Dobele G., Andersone A., Gawdzik B., Lindström M.E., Sevastyanova O., [Carbon Adsorbents from Industrial Hydrolysis Lignin: The USSR/Eastern European Experience and Its Importance for Modern Biorefineries](#), *Renewable and Sustainable Energy Reviews*, **57**: 1008–1024 (2016).
- [28] Smolenkov A.D., Shpigun O.A., [Direct Liquid Chromatographic Determination of Hydrazines: A Review](#), *Talanta*, **102**:93–100 (2012).
- [29] Kosyakov D.S., Pikovskoi I.I., Ul'yanovskii N.V., Kozhevnikov A.Yu. [Direct Determination of Hydrazine, Methylhydrazine, and 1,1-Dimethylhydrazine by Zwitterionic Hydrophilic Interaction Liquid Chromatography with Amperometric Detection](#), *International Journal of Environmental Analytical Chemistry*, **97**: 313–329 (2017).