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Remediation of soil contaminated by toxic rocket fuel components using modified carbon–mineral adsorbing material produced from shungite rock modified with Mn⁴⁺ and Fe³⁺



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ABSTRACT

The study develops a novel catalytic adsorption material for remediation of soils contaminated by toxic rocket fuel components (RFC). Modified carbon–mineral material (MCMM) sorbent is produced using shungite rock and modified using iron (III) chloride and manganese (IV) oxide. MCMM production process is developed, and MCMM remediation efficiency is tested using soil samples from rocket separating parts impact sites with RFCs contamination. The structure of shungite and the physicochemical parameters of MCMM, the soils contamination at the impact areas of the rocket separating parts, and the ways rocket fuel components transformation in the soil were investigated. The obtained MCMM showed the efficiency of sorption and catalytic decomposition of the rocket fuel transformation products and determined the optimal conditions for remediation. The index of soil detoxification at a concentration of the analyzed decay products is from 0.1 mg/kg to 3.21 mg/kg is from 81.1 to 98.8%.

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1. Introduction

The rocket and space industry is becoming the type of activity that determines the general potential of a country and its scientific, technical, educational, and social capabilities. At the same time rocket and space industry has broad negative influence on the environment (Kompanietz, 2001). Space launch site Baikonur which is based on the territory of The Republic of Kazakhstan incites the aggravation of environmental pollution problems caused by rocket fuel components (RFCs) and products of their transformation at the launch sites as well as the impact areas of the separated parts of the carrier rocket (SPCR) (Kopack, 2019; Sand, 1972). Each falling SPCR still contains sufficient amount of unreacted rocket fuel components and oxidizer upon impact to the ground. According to the telemetric data (Ponomarenko, 1995), the amount of fuel components remaining in the tanks varies between 0.3 and 2.0 tons, and the amount of oxidizer left in the tanks

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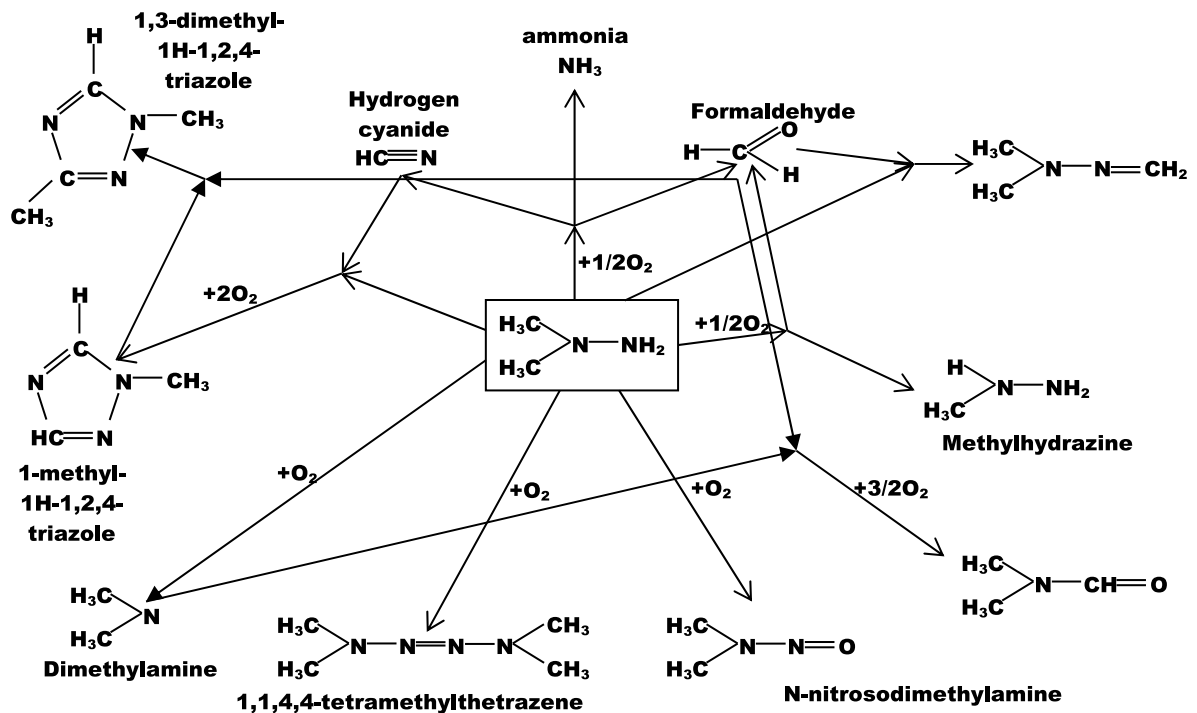


Fig. 1. UDMH transformation upon exposure to an environment.

varies between 1.2 and 4.0 tons. Hence, a drop of rocket's first stage from an altitude of 50–120 km is followed by a spill of 0.6–2.0 tons of unsymmetric dimethylhydrazine (UDMH) and 1.4–6.0 tons of nitrogen tetroxide into the soil and water bodies. Meanwhile, the maximum permissible concentration of UDMH is $1 \mu\text{g}/\text{m}^3$ or $1 \text{ kg}/\text{km}^3$ of air. Evaporation of 2 tons of UDMH poisons up to $200,000 \text{ m}^3$ of air and the UDMH spill to the ground poisons scope of a surface with a radius of 200–300 m at impact area (Bushmarin et al., 1996). In places of SPCR impact, where fuel spills occur, local soil contamination with contrasting concentrations are formed. Secondary contamination occur due to relocation of SPCR debris which surfaces contain rocket fuel remnants (Permenev, 2006).

Typically, pollution with RFCs has localized pattern, despite the possibility of the pollutants to spread over large areas. This is explained by low mobility of UDMH when adsorbed by the soil and its further rapid dilution of component to safe concentrations (during rains and floods). One of the ways UDMH is carried away beyond the impact areas is ground and surface water.

Previous gas chromatographic analysis with an Agilent G890N5973N mass spectrometric detector and liquid chromatography with a diode array detector, shows that UDMH which is entering the ecosystem can be partially transformed into N-nitrosoamines (NDMA), tetramethyltetrazene (TMT), methylmethylen hydrazine (MMH), 1,3-dimethyl-1H-1,2,4-triazole (DMT), 1-methyl-1H-1,2,4-triazole (MT), N,N-dimethylformamide (DMFA), dimethylamine (DMA) and other nitrogen containing substances with pronounced carcinogenic properties (Rodin et al., 2012; Kenessov et al., 2012). Fig. 1 demonstrates the transformation routes of UDMH when exposed to air oxidation.

Due to carcinogenic properties, localization and detoxification of areas contaminated with UDMH are time-sensitive issues for restoring environmental-balance and returning the soil for agricultural activities. Various chemical, physicochemical, thermal, mechanical, microbiological methods have been proposed for detoxification of contaminated with UDMH soil and its oxidation products (Zhubatov et al., 2017). However, many of these methods show reduced efficiency and applicability due to climatic conditions common for locations such as Kazakhstan.

One of the promising methods is a combination of sorption and catalytic decomposition methods. This combined method is used for localization of spills and for purification of natural and wastewater (Kozhevnikov et al., 2017a,b; Ye et al., 2020). Search of affordable and effective materials, improvement of technologies for regeneration and utilization are the main development trends. The amount of UDMH entering the atmosphere and water streams can be significantly reduces by using sorption and catalytic materials. Various natural (peat, natural aluminosilicates) and synthetic (activated carbons, ion-exchange resins, polymer materials, modified lignins, etc.) substances are used as sorbents (Kozhevnikov et al., 2017a,b) and they also can be applied for solving other environmental pollution issues. For instance, Ye et al. suggest magnetic biochar with porosity and graphitization for removal of metal from the microplastics, as a result, heterogeneous catalysis of persulfate (PS) activated by PGMB achieved the decomposition of organics, with the decrease of more than 60% of the attached Pb on the surface of microplastics (Ye et al., 2020). However, soil contaminated by rocket fuel and its

transformation products can be removed with the help of these methods only up to 80% at best. After purification with sorbents, it is necessary to carry out additional purification using other methods (for example, microbiological) in order to reduce the level of UDMH pollution below the maximum permissible concentration (Liao et al., 2016).

Kosyakov et al. studied the effect of an oxidizer and a catalyst on the transformation products of 1,1-dimethylhydrazine in water and soil (Kosyakov et al., 2019). Fenton's reagent, KMnO_4 , HOCl , H_2O_2 in the presence of Cu^{2+} and Fe^{3+} catalysts were used as an oxidizing agent. The work demonstrated that none of the investigated oxidizing reagents provided complete conversion of RFCs into safe compounds. Bromberg et al. proposed an efficient method for the decomposition of 1,1-dimethylhydrazine with brominated polymer matrices (Bromberg et al., 2014).

Ye et al. developed modified material by nitrogen doping of biochar derived from filaments biomass (NRBF) of Ramie, which is used for improving the catalytic performance for peroxydisulfate (PDS) activation, and achieving 4.5 times higher decomposition rate of tetracycline than non-modified biochar (Ye et al., 2021).

Based on the facts, searching for effective detoxification materials and methods with simultaneous sorption and catalytic properties, that would be capable of restoring soils exposed to negative influence from rocket and space activities has become essentially crucial issue. To obtain this kind of sorbent-catalysts, we propose to use carbon-mineral natural shales called shungite rocks, which are practically considered to be unclaimed in Kazakhstan. Shungite carbon is petrified oil, or amorphous, non-crystallizing, fullerene-like (i.e., containing certain regular structures) carbon, its content in rocks is from 0.5% to 50%, it also contains aluminosilicates, alkali metal oxides and trace amounts of noble and rare earth metals (Berezkin, 2005; Efremov, 2010; Melezhihik et al., 1999). The presence of such a set of elements and the structure of shungite determine its unique technological and rheological properties. Shungite is characterized by a high level of heterogeneity of the chemical composition, as well as structural parameters of the carbon and mineral components. Variations in the content of carbon and minerals in shungite rocks are closely related to the heterogeneity of their structure, previously revealed at the macro and micro levels (Gusmão et al., 2017). Also, when using shungite as a basis for a catalyst, its rare earth and rare metal mineralization is of considerable practical interest. In addition, the prospects for using shungite in the preparation of catalysts is associated with its main distinctive property – the ability to wet with non-polar liquids and water, i.e. its diphilicity, which is again characterized by the presence of carbon and mineral components in the composition of shungite.

Shungite is a complex sorbent and a natural catalyst or catalyst carrier that is of a great interest in chemical technology; Shungite concurrently exhibit properties of carbon and silicate materials (Gusmão et al., 2017; Mooste et al., 2021; Atchabarova et al., 2013; Tokpayev et al., 2015). While being an excellent sorption material, it can be used to purify wastewater from oil products and heavy metals in practice (Ul'yanov et al., 2018; Nechipurenko et al., 2010; Aubakirova et al., 2020).

The aims of this study includes development of process for production of MCMM using shungite, production of MCMM, and examining MCMM detoxifying effect of MCMM on soil contaminated with RFC and its components. Consequently, the corresponding tasks include shungite enrichment, development of a process for production of modified carbon-mineral material sorbents (MCMM), determination of physical and chemical parameters of MCMM, IR spectroscopic and X-ray diffraction analyzes of shungite rocks, soli analysis, detoxification soil using MCMM, and determine the amount of RFC after detoxification with MCMM.

2. Materials and methods

2.1. Enrichment of shungite rocks

Shungite rocks are found in both natural deposits and in tailing dumps after enrichment and extraction of polymetallic ores. In Bakyrchik deposit located in Zharminsky region of East Kazakhstan, a contour of the ore body contains total estimated reserves of over 30.0 million tons. These volumes are considered sufficient for industrial use. The physical and chemical properties of Shungite rock from Bakyrchik deposit had been studied elsewhere (Efremov et al., 2013).

Depending on the depth of occurrence and natural forming factors, natural strata occurring in the ore body is not uniform in its chemical composition (Nechipurenko, 2007). Uniformity of chemical compositions and particle size distribution are mandatory requirements for natural materials used in technological processes. For instance, the carbon content of Bakyrchik shungite ore ranges from 6.5 to 43.5%, therefore, to obtain representative samples and increase the overall carbon content, the samples were treated with flotation enrichment. The enrichment was carried out on a flotation machine of FM-2M series. The shungite ore was crushed and sieved to a size less than 74 μm . During flotation experiments kerosene was used as a collector, which enhances the adhesion of hydrophobic ore particles to air bubbles, the Flotol series commercial flotation agent, and the regulator-depressant of the hydrophilic part of the ore is liquid glass. This combination of flotation reagents allowed to enrich the ore just within single operation and to obtain shungite with carbon content of 44.9%, the enrichment wastes had carbon content of 1.1%. The enriched shungite yield was 40.6%. The detailed shungite enrichment procedure can be found elsewhere (Efremov et al., 2013; Nechipurenko, 2007).

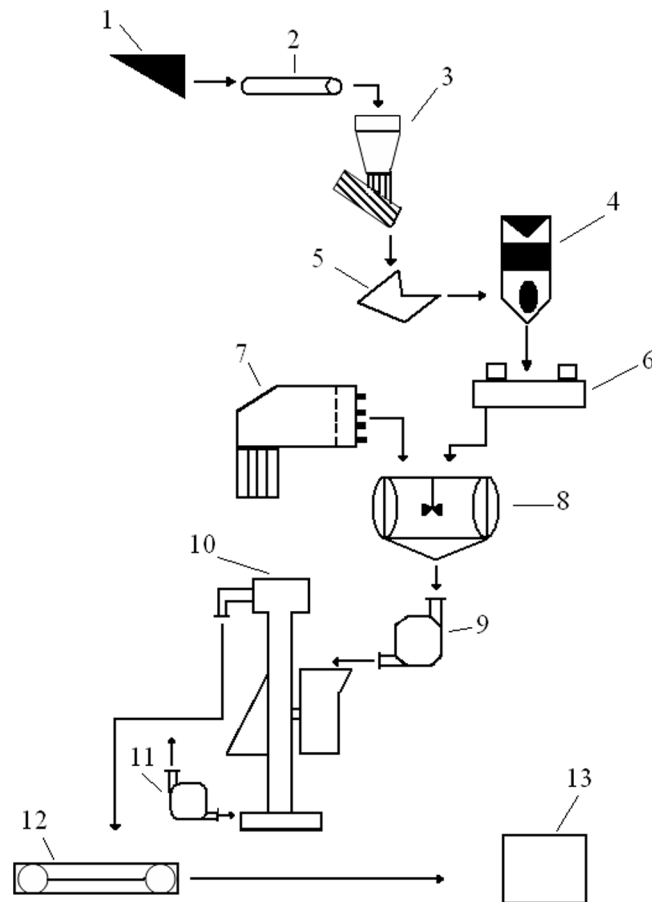


Fig. 2. Technological scheme for obtaining MCMM.

2.2. Production of modified carbon–mineral material sorbents (MCMM)

A process for production of MCMM was developed. The process flowsheet diagram (PFD) of the process is shown in Fig. 2. The shungite ore (1) is supplied through the transporter (2) into the crusher (3). The crushed ore is sieved and conveyed to the mill. Then ore is conveyed to the air separator (6). Milled ore is mixed with floating agent in the mixer (8) to form an ore-water slurry. The slurry is supplied through the pump into the flotation machine (10) equipped with a pump (11) which supplies the enriched shungite to the modifying unit (12) which produces the final MCMM product (13). Enriched shungite ore was air dried prior using it to produce MCMM. MCMM was prepared on the basis of shungite carbon concentrate, which was a homogeneous powdery mass, with a fineness of less than $74\ \mu\text{m}$, black, air dry. The average chemical composition of the enrichment process products is: C (40.0%); SiO_2 (37.7%); TiO_2 (0.2%); Al_2O_3 (7.8%); Fe_2O_3 (3.6%); CaO (2.8%); MgO (2.7%); Na_2O (0.3%); K_2O (3.7%).

The final stage of MCMM production is a modification (12) with transition metal ions. Modifying agents were selected on the basis of X-ray spectral analysis of soils, where it was found that the ions of manganese and iron are contained in the soil in a rather small amount. Therefore, manganese and iron were chosen as modifiers, the most active oxidizing agents promoting the destruction of UDMH with higher MPC values.

Dry salts of transition metal ions, iron (III) chloride for the first series and manganese (IV) oxide for the second series of carbon catalysts were used as modifying agents. In both cases, the amount used was 5% of the total sorbent mass. Manganese and iron are also highly active oxidants capable of degrading UDMH and the products of its transformation to amines which have higher MPC to the native soils of the SPCR fall area. The amount of modifying agents, iron chloride (III) and manganese oxide (IV), was determined based on the chemical composition of the enriched shungite. Besides amorphous carbon, shungite contains metal oxides which also have catalytic effect. The structure of manganese oxide (IV) can substantially influence the adsorption and catalytic properties of the composite material (Ivanets et al., 2018, 2017a). The manganese oxide (IV) used in this study had a layered structure. Production of manganese oxide (IV) with tunnel structure requires additional processing which is not the subject in this work.

Table 1

Coordinates where the representative samples of soils from the places where the first stages of the Proton launch vehicle fell.

№ Zone	Shape of the area	Coordinates of the center	Axis size	Large axis azimuth, deg.	Area, Thousand ha
U-24 (Impact area t#15/25)	elliptic	47°20'30" 66°46'30" 47°14'00" 66°23'00"	27 × 18 60 × 30	65 65	160

The shungite sorbent was modified by mechanical interaction of the enriched shungite with the catalysts until it is uniformly distributed over the entire volume of the batch. The mixture was pre-moistened for a more efficient distribution of modifying agents throughout the volume of the batch. Then the mixture of enriched shungite and catalyst were granulated to produce carbon-catalyst granules with size of 0.5 ÷ 2.0 mm. Granulation was carried out by passing a paste like carbon-catalytic material through an extruder with die holes of 2.0 mm, followed by drying the granules for 2.5–3.0 h at a temperature of 105 °C in a drying oven. This operation was necessary for the subsequent separation of the sorbent from the soil samples. Similar operations are used for preparation of carbon-catalytic sorbents when using iron chloride (III) and for manganese oxide (IV).

2.3. Determination of physical and chemical parameters of MCMM

To determine the specific surface area of MCMM we used the dynamic method of thermal desorption (Efremova and Korolev, 2003; GOST 25699.4-90, 1990), the essence of which is to change the thermal conductivity of a gas flow (helium or hydrogen with the addition of nitrogen or argon) passing through a tube with a measured sample and determining the amount of a mixture of gases (argon 95% and helium 5%), adsorbed on the sample from the gas mixture when it is cooled with liquid nitrogen and desorbed when the sample is subsequently heated to a temperature of 100° C. Similar approach with carbon black),

To determine the sorption capacity of MCMM with respect to RFCs, a weighed portion of the sorbent was placed in a container with a tightly ground stopper, and a solution of UDMH with a given concentration was added in a ratio of solid and liquid phases of 1:5. After 3 h of stirring and 24 h of settling, the liquid and solid phases were separated. The method for determining moisture content (GOST 27314-91, 1991) is based on drying the test samples in an oven at 160 ± 5 °C, weighing and calculating the moisture content from the difference.

Measurement error in determining the total moisture was 0.3% and error in determining the moisture of analytical sample was estimated to be 0.2% with a confidence level of 95%.

In order to determine total volume of pore by acetone adsorption, MCMM sample was placed into weight measuring cylinder with a capacity of 1*10⁻⁴ m³ (internal diameter 0.025 m). The filling of the cylinder to the mark of 1*10⁻⁴ m³ was carried out in portions of 15*10⁻⁶–20*10⁻⁶ m³, with the compaction of the sorbent after adding each portion to (300 ± 10) kg/m³. The cylinder with the sorbent was weighed to the nearest 0.01 g and filled with acetone to a constant level of acetone above the sorbent layer. After 30 min, the excess acetone was drained off and the cylinder with the sorbent is weighed. Acetone porosity X (in volume%) was calculated by the formula:

$$X = \frac{(G_1 - G_2) * 100}{\rho V} = \frac{G_1'' - G_2}{\rho} \quad (1)$$

where G₂- weight of the cylinder with sorbent before impregnation, kg;

G₁- weight of the cylinder with a sorbent impregnated with acetone, kg;

ρ - density of acetone at the temperature of the experiment, kg/m³;

V - 1*10⁻⁴ m³ - the volume of the active sorbent.

IR spectroscopic analysis was performed on an FTIR spectrometer (Avatar-370, Thermo Nicolet Co.) in the spectral range of 4000–350 cm⁻¹ with the sample in the form of a tablet. X-ray diffraction (XRD) analysis of shungite rocks was carried out using an XRD (D8 Advance, Bruker), α-Cu, tube voltage 40 kV, current 40 mA.

2.4. Soil analysis

Samples of soil for the experiments were collected from areas contaminated by RFCs in locations of SPCR first stage fall sites and perimeter of the impact area. Positional impact area #15/25 of the first stages of the Proton launch vehicles is located in the southwest of Ulytau district of Karaganda region of the Republic of Kazakhstan. The coordinates of the centers and areas of the fall sites are given in Table 1.

The results of field studies on diagnosis of the soil cover showed that the territory of impact area 15/25 was represented mainly by medium and heavy loamy, as well as clayey soil types. Therefore, for the study, we selected the sites of the SPCR fall where this type of soil was typical.

To obtain representative samples, the soil taken from the positional region of the SPCR fall with UDMH concentrations from 0.8 mg/kg to 4.5 mg/kg (which corresponds to 8–45 MPC for soils) were thoroughly mechanically mixed until a homogeneous mass was obtained.

Table 2
Physical and chemical properties of MCMM.

Indicator name	MCMM Mn ⁴⁺	MCMM Fe ³⁺
Bulk density, g/cm ³	1,24	1,2
Moisture content, %	4,5	4,79
Specific surface, m ² /g	140	140
Total pore volume, cm ³ /g	0,452	0,450
Sorption capacity for iodine, mg/g	32	29
Porosity, %	35,58	35,50

2.5. Soil detoxification from RFCs

To find the optimal conditions for detoxification of the studied soils the influence of a number of factors on the sorption catalytic decomposition of UDMH and its transformation products were considered: soil moisture, the ratio of soil-MCMM, the time of soil contact with the sorbent, and temperature. Beakers with a volume of 1000 ml were placed 300 g of soil and MCMM in predefined ratios. The soil moisture was as close as possible to the field conditions. The soil was thoroughly mixed with MCMM throughout the volume and kept in the open air at room temperature for a specified period of time. The time intervals through which the sampling was carried out were: 1, 6, 16 and 24 h. After the expiration of the control time intervals, soil samples after detoxification were taken to determine the content of RFCs and its transformation products. The soil was separated from the granular sorbent using the sieve method. To eliminate inaccuracy in the purity of the experiment and to take into account the effect of aeration under these conditions, a control experiment was performed without MCMM. For this purpose, contaminated soil was infused into beakers of equal volume and similarly to the experimental samples, it was subjected to mechanical mixing, then these samples were analyzed for content of RFCs and its transformation products. This operation was necessary to take into account the loss of RFCs from the soil due to oxidation with air oxygen. The time intervals for taking control samples, as in the experimental samples, were 1, 6, 16 and 24 h.

2.6. Determination of RFCs and their transformation products in soil samples

RFCs and their transformation products content in soil analysis method was based on the acidic extraction RFCs and transformation products from the soil, alkaline distillation of steam in acetic acid solution, interaction with n-nitrobenzaldehyde and determining product derivatization by liquid reverse phase chromatography with spectrophotometric detection at wavelength – 390 nm (Nauryzbaev et al., 2005; Ul'yanovskii et al., 2015; KZ.07.00.00571-2006, 2006). Investigation of materials sorption characteristics can be conducted using kinetic and thermodynamic methods or using spectral analysis methods, such as X-ray fluorescence, atomic absorption spectroscopy, and gas chromatography analysis (Ivanets et al., 2017b). Since one of the aims of the work is to evaluate the efficiency of sorption and catalytic decomposition of UDMH and its transformation products. The concentrations of RFCs and transformation products were measured using a gas chromatograph Agilent 6890N/5973N with a mass spectrometric detector and using a liquid chromatograph with a diode array detector, a four-channel gradient pump, and an Agilent +1100 series microdegasser.

The soil detoxification index was calculated using the formula:

$$\varepsilon = \frac{C_0 - C}{C_0} * 100\% \quad (2)$$

C_0 - the initial content of RFCs in the soil, mg/kg;

C - content of RFCs in soil at control time intervals, mg/kg.

3. Results and discussion

3.1. Physical and chemical properties of the MCMM and shungite

For effective use of MCMM Fe³⁺ and MCMM Mn⁴⁺, understanding of their physicochemical sorption characteristics, such as specific surface area, pore volume, porosity and sorption capacity for iodine are essential. The material should have a relatively developed surface and sorption data. Attributes of the porous structure of MCMM (specific surface area, total pore volume and porosity) were analyzed by the BET method based on nitrogen adsorption at 77 °K. The results of the analysis are described in Table 2. Table 2 shows that MCMM Mn⁴⁺ has higher sorption capacity in relation to iodine. The rest of the parameters of examined MCMM samples are similar because both originated from the same initial material.

IR spectroscopic study of MCMM made possible to obtain information on the structure of shungite carbon and the qualitative composition of functional groups on their surface. According to the absorption spectra (Fig. 3), the samples contain: Muscovit KAl₂[(OH,F)₂AlSi₃O₁₀] - 3629, 3434, 1622, 1031, 832, 756, 537, 475, 411 cm⁻¹; Quarz SiO₂ - 1081, 798, 778, 695, 397, 374 cm⁻¹; Albit Na[AlSi₃O₈] - 1165, 987, 742, 475 cm⁻¹; Ankerit CaFe(CO₃)₂ - 1424, 872, 727 cm⁻¹, In

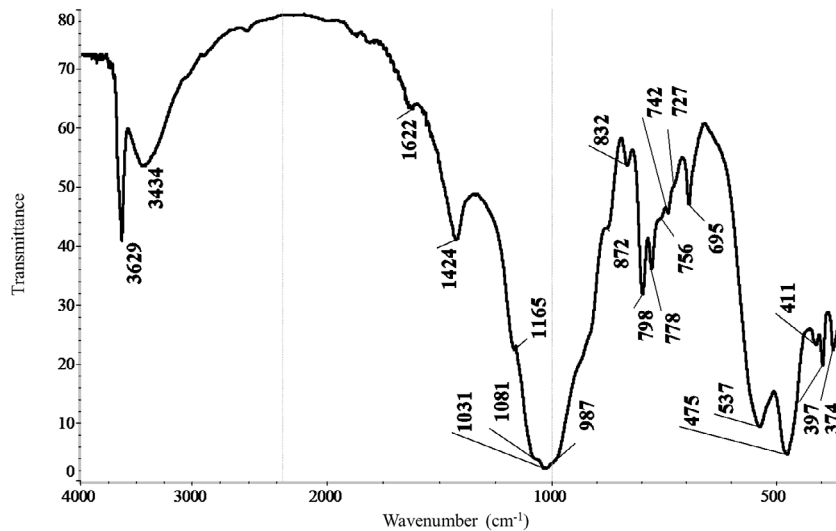


Fig. 3. IR spectrum of MCRM.

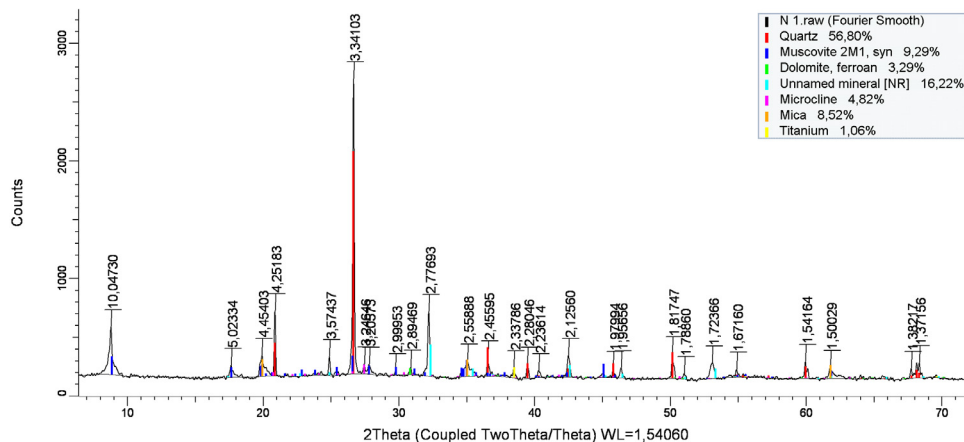


Fig. 4a. X-ray diffraction analysis of shungite (C ~ -12.0%)

the long-wavelength region of the spectrum, there is a manifestation of stretching vibrations ν OH – 3434 cm^{-1} , HOH – 1622 cm^{-1} .

Information on the mineralogical composition of the carrier shungite is necessary in order not to disturb the existing natural soil balance in the areas where the SPCR falls during and after the field work on soil detoxification. In this regard, X-ray diffraction (XRD) studies of shungite and its concentrate were carried out.

The processing of the obtained XRD data patterns and the calculation of interplanar distances were carried out using the EVA software. Sample decoding and phase search were carried out using the Search/match program using the PDF-2 powder diffractometric data base.

XRD investigation of natural shungite ore showed that the analyzed samples were composed of the carbonaceous material and mineral components, the quantitative content of which varied depending on the enrichment of carbon (see Figs. 4a and 4b).

3.2. Contaminated soil analysis

As a result of the UDMH oxidation, the formation of other chemical compounds, both linear and cyclic, is possible. These reactions are accompanied with the formation of intermediate compounds that have low MPC threshold and pose a threat to the environment. Table 3 shows the content of UDMH and its decomposition products in three soil samples extracted from the impact area (IA#25). Samples were thoroughly mixed producing an averaged sample. The content of UDMH and its decomposition products were also determined in the averaged sample. Based on the quantitative data obtained on the

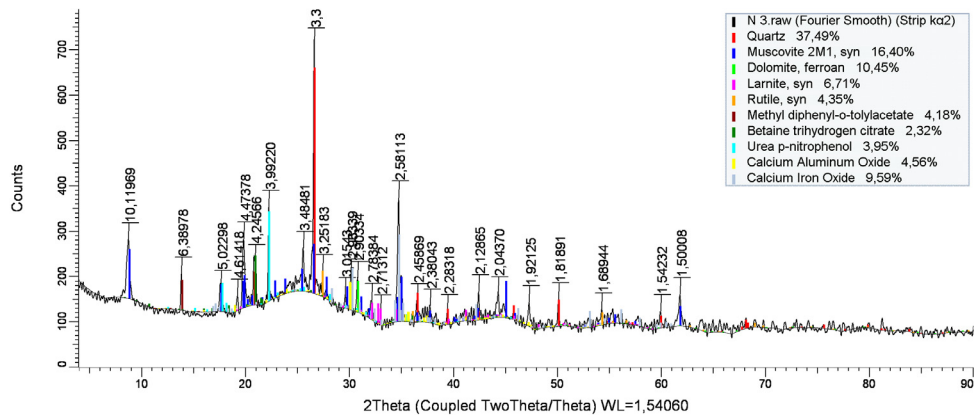


Fig. 4b. (b) X-ray diffraction analysis of shungite concentrate (C ~ – 40.0%).

Table 3

Content of UDMH and products of its transformation in the studied soils.

	Content, mg/kg				
	UDMH	NDMA	DMFA	MT	DMT
1	0.902	0.430	0.166	0.620	0.531
2	2.411	0.330	0.612	0.421	0.302
3	3.894	0.495	0.101	0.142	0.377
Averaged	3.450	0.484	0.131	0.256	0.377
	0.1*	–*	0.7*	0.1*	–*

*Maximum permissible limit in soil

Table 4

Influence of the concentration of transition metals on the shungite carrier in the detoxification process of soils contaminated with UDMH (the duration of the detoxification process is 24 hrs, the initial concentration $C_{\text{UDMH}} = 3.450$ mg/kg).

Modifier Fe^{3+} or Mn^{4+} , wt%	C_p , mg/kg	Index of detoxification, %
5 - Fe^{3+}	not found	100%
3 - Fe^{3+}	0,141	96%
1 - Fe^{3+}	0,342	90%
5 - Mn^{4+}	not found	100%
3 - Mn^{4+}	0,150	96%
1 - Mn^{4+}	0,373	89%

content of UDMH conversion products in soil samples, it can be concluded that the samples mainly contain conversion products such as NDMA, DMFA, MT, and DMT. The formation of these products can be explained by incomplete oxidation of UDMH in the soil.

In further studies, averaged samples, extracted from soil contaminated by RFCs and their decay products were used.

It was experimentally established that soil moisture is in the range of 0%–10%, and it insignificantly affects the detoxification process and averages 97.0% with the initial soil contamination with UDMH in the amount of 3.21 mg/kg.

3.3. Detoxification of soil from UDMH and its transformation products

The concentration of modifying catalytic agents added to the MCMM influences UDMH oxidation reaction rates and thus also influences the detoxification index of the soil. Table 4 describes the effect of Fe^{3+} or Mn^{4+} wt% in MCMM on detoxification of soil. The amount of transition metal salts on the shungite carrier was selected experimentally for maximum destruction of UDMH in samples, which have UDMH concentrations exceeding the MPC by more than 30 times. This samples correspond to the level of pollution in the areas where the first stages of the carrier rocket fall (Zhubatov et al., 2017). It was found that the most effective is MCMM with 5% content of metal salt.

An important parameter of detoxification is the soil-to-MCMM ratio and their contact time. Analysis of the experimental data showed that MCMM with Mn^{4+} , as well as MCMM with Fe^{3+} , exhibit a rather high activity in the process of soil detoxification from UDMH even when the ratio of soil-to-MCMM is 9:1. The detoxification index removing UDMH after 48 h reaches values close to 100%. In this case, the main process of detoxification takes place in the first 24 h. As a result, for the reproducibility of experimental results and, if necessary, taking into account the relative error, the main

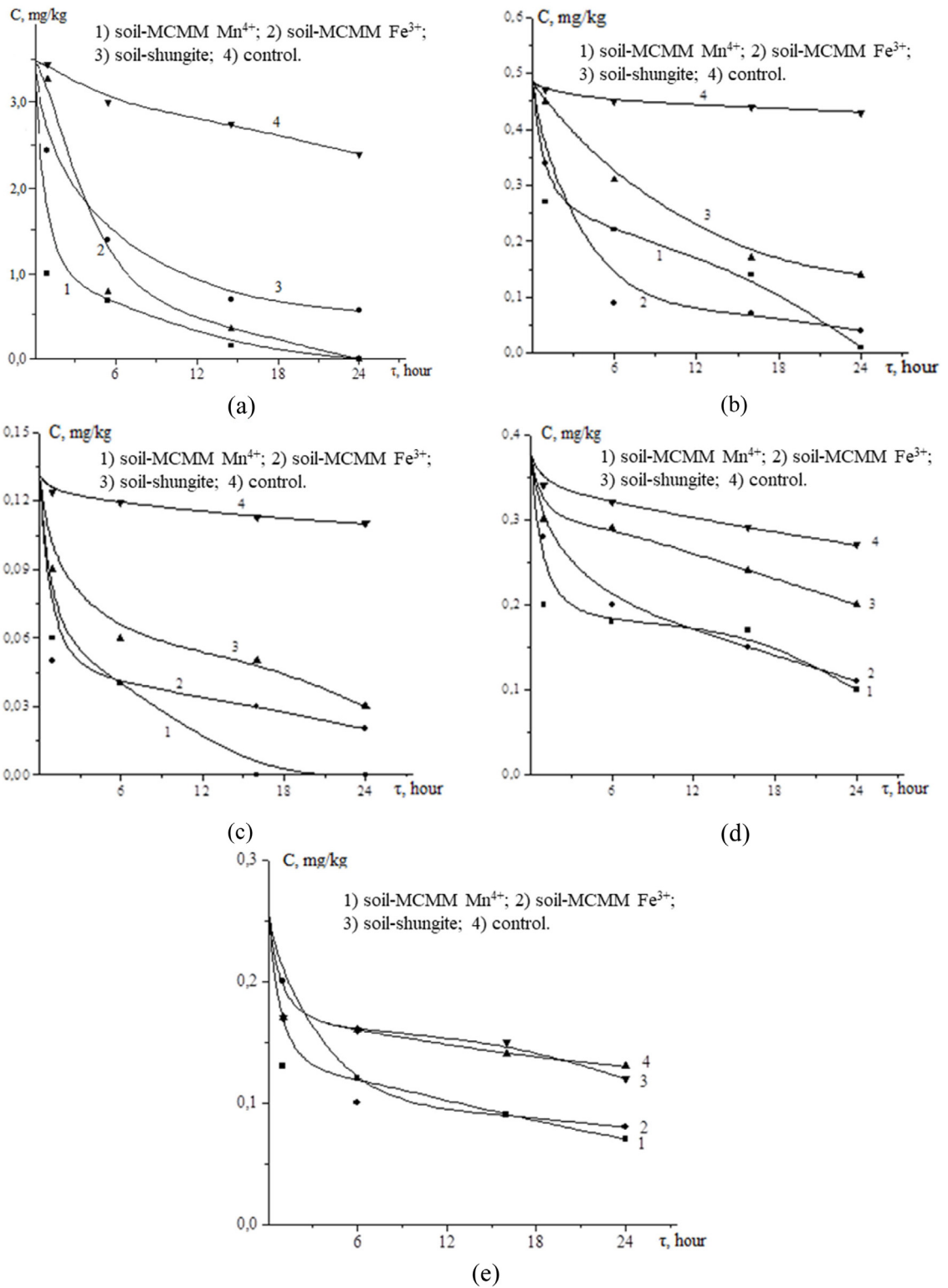


Fig. 5. Influence of the detoxification material and contact time to detoxification of soil: (a) UDMH: $C_0 = 3,450$ mg/kg; (b) NDMA: $C_0 = 0,484$ mg/kg; (c) DMFA $C_0 = 0,131$ mg/kg; (d) DMT $C_0 = 0,377$ mg/kg; (e) MT $C_0 = 0,256$ mg/kg.

parameters in the studies were subsequently taken: moisture – no more than 10%, the ratio of soil-to-MCMM is 9:1, detoxification process time 24 h, room temperature ($22 \pm 2^\circ\text{C}$). For comparison, the detoxification activity of unmodified shungite was also studied. The Fig. 5 describes detoxification of soil from UDMH (Fig. 5(a)) and its decomposition products, including NDMA (Fig. 5(b)), DMFA (Fig. 5(c)), DMT (Fig. 5(d)), and MT (Fig. 5(e)). The initial concentration of UDMH was 3,450 mg/kg, NDMA was 0,484 mg/kg, DMFA was 0,131 mg/kg, DMT was 0,377 mg/kg, and MT was 0,256 mg/kg. The Fig. 5 compares detoxification using MCMM Mn^{4+} and MCMM Fe^{3+} . In order to determine the effect of modification MCMM was compared with unmodified enriched shungite. Comparison demonstrates that both MCMM Mn^{4+} and MCMM Fe^{3+} are more effective than unmodified enriched shungite. The detoxification index of soil from UDMH and its decomposition products at given initial concentrations was between 81.1% and 98.8%. MCMM Mn^{4+} performed slightly better than MCMM Fe^{3+} in removing UDMH at first 18 h, but they both removed almost all of UDMH in 24 h. MCMM Mn^{4+} also was more effective in removing NDMA. Both MCMM Mn^{4+} and MCMM Fe^{3+} performed less effectively in removing DMT and MT, but they clearly demonstrated MCMM performs better than unmodified shungite. The influence of the simple aeration process is within 30%. Complete oxidation of RFCs and its components adsorbed on MCMM occurs mainly under the action of atmospheric oxygen in the presence of catalytically active agents. Thus, it has been proved that when using Mn^{4+} MCMM and Fe^{3+} MCMM for the processes of decontamination of soils contaminated with RFCs, an almost complete recovery of soils subject to rocket and space activity occurs.

4. Conclusion

1. It has been established that the studied shungite rock is a multiphase material, which contains carbonaceous and mineral components.

2. A process for enrichment of shungite rock was developed. Enrichment process uses kerosene (0.25 kg per ton of shungite) and a foaming agent – Flotol B (0.3 kg per ton of shungite). The enriched shungite composition was C (40.0%); SiO_2 (37.7%); TiO_2 (0.2%); Al_2O_3 (7.8%); Fe_2O_3 (3.6%); CaO (2.8%); MgO (2.7%); Na_2O (0.3%); K_2O (3.7%).

3. A process for production of MCMM Mn^{4+} and MCMM Fe^{3+} was developed using enriched shungite as raw material and 5 wt% of iron (III) chloride and manganese (IV) oxide as modifying agents.

4. MCMM Mn^{4+} and MCMM Fe^{3+} were tested for detoxification of soil samples containing UDMH and its transformation products, including NDMA, DMFA, MT, and DMT. The ratio of soil-to-MCMM was 9:1. MCMM Mn^{4+} and MCMM Fe^{3+} were compared with non-modified shungite and soil without detoxifying agents. The detoxification index of the soil contaminated with UDMH and its transformation products at these concentrations varied from 81.1 to 98.8%.

5. The developed technology of detoxification promotes the decomposition of RFCs to non-toxic components. MCMM developed in this study does not use strong oxidizers, such as Fenton, KMnO_4 , or HOCl, which reduces disturbance to the environmental balance. The use of MCMM can be recommended for the remediation of contaminated soil areas, as well as in the places of SRT spills as a result of accidental releases, which will contribute to solving a number of environmental issues.

CRedit authorship contribution statement

Sergey Efremov: Conceptualization, Funding acquisition, Investigation, Writing – original draft. **Sergey Nechipurenko:** Conceptualization, Project administration, Writing – review & editing, Investigation. **Diyar Tokmurzin:** Investigation, Writing – original draft, Writing – review & editing, Visualization. **Aigerim Kaiaidarova:** Investigation. **Sergey Kalugin:** Investigation. **Khaidar Tassibekov:** Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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