

Synthesis of Chemical Adsorbent for Purification of Heavy Oil Residue

Galymzhan Maldybayev^{1,2*}, Roza Shayakhmetova¹, Saule Nurzhanova³, Rustam Sharipov², El-Sayed Negim^{2,4}, Aliya Alimzhanova¹, Petr Osipov¹, Anar Mukhametzhanova¹, Anwar Usman⁵

¹National Center on complex processing of mineral raw materials of the Republic of Kazakhstan, 67 Jandossov Str., Almaty 050036, Republic of Kazakhstan

²School of Materials Science and Green Technologies, Kazakh-British Technical University, St. Tole Bi, 59, Almaty 050000, Kazakhstan

³Sokolsky Institute of Organic Catalysis and Electrochemistry, 142 Kunaev St., Almaty 050010, Republic of Kazakhstan

⁴School of Petroleum Engineering, Satbayev University, 22 Satpayev Street, Almaty 050013, Kazakhstan

⁵Department of Chemistry, Faculty of Science, University Brunei Darussalam, Jalan Tungku Link, Gadong BE1410, Brunei Darussalam

Abstract. This study aimed to investigate synthesized wollastonite based on amorphous silicon dioxide and calcium carbonate as adsorbent for cleaning hydrocarbon feedstock from heavy organometallic compounds and sulfur. During the analysis, physicochemical parameters including the specific surface area and intensity of synthesized wollastonite were determined. The results showed that the optimal temperature zone for demetallization of hydrocarbon raw materials was 653 - 683 K, with a contact time of 60 minutes, and pressure of 8 - 10 atm. Furthermore, the content of vanadium, nickel, iron, and sulfur was found to decrease from 540 to 52 µg/kg, 50 to 26 µg/kg, 50 to 12 µg/kg, and 3.50% to 2.39%, respectively.

Keywords: Adsorbent; Asbestos waste; Demetallization; Heavy oil; Sulfur

1. Introduction

Cracking of oil in zeolites is one of the most significant industrial applications in oil refining. In this field, attention is focused on developing catalytic systems using nanosized zeolites and micro-mesoporous materials. The wide use of zeolites as a valuable tool in nanotechnology is attributed to their unique properties, such as nanoscale of cavities, capacity for precise arrangement of active centers, selectivity, and directional effect on chemical groups of molecules (Johansson *et al.*, 2023; Ulfiati *et al.*, 2022; Ongarbayev *et al.*, 2020; Li *et al.*, 2020; Attia *et al.*, 2020; Shang *et al.*, 2016; Jo *et al.*, 2014).

Recently, various inorganic substances such as hydroxides, silicates, phosphates, and aluminosilicates, have gained significant attention. This is due to the widespread availability of inorganic substances, along with high thermal and chemical resistance, serving as effective and accessible sorbents. Although the activity of sorbents containing zeolites depends on the concentration of hydrogen ions and mobility, regulation can be

*Corresponding author's email: galimjan_87@mail.ru, Tel.: +77071414241
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made by introducing polyvalent cations into the adsorption complex, with electron-accepting properties (Prihadiyono *et al.*, 2022; Farghadani and Mahdavi, 2022; Baikonurova *et al.*, 2021; Sudibandriyo and Putri, 2020; Zarraoa, Gonz'alez, and Paulo, 2019; Kamal, Razzak, and Hossain, 2016; Markametova, *et al.*, 2014).

Sorbents are generally obtained from natural minerals and secondary raw materials, such as waste from extraction plants, which mainly contain silicate and aluminosilicate non-metallic minerals. Moreover, obtaining effective sorbents based on anthropogenic raw materials can solve both technological issues by expanding the range of products and creating innovative technologies, as well as ecological problems through purification and disposal of waste (Suryanti *et al.*, 2023; Solouki, Jaffer, and Chaouki, 2022; Li *et al.*, 2019; Zhang *et al.*, 2016; Galarneau *et al.*, 2014; Milinchuk and Shilina, 2010). Due to the huge amount of waste produced in various industries, there is a need for asbestos mineral extraction plants to explore innovative technological solutions focusing on the construction and diversification of materials for other purposes. This strategic shift can expand the range of manufactured products and solve environmental problems for the processing of deposited waste (Baigenzhenov *et al.*, 2024; 2022; Kraus *et al.*, 2018; Jenifer, 2015). Recent study has described the methods of obtaining molecular sieves and zeolites from rice husks (Zainal *et al.*, 2024; Zharmenov *et al.*, 2018; Yefremova *et al.*, 2016; Jo *et al.*, 2015), showing properties comparable with commercial types. Therefore, the development of technologies for deep processing of heavy oil with high metal and sulfur content is essential, requiring the search for new efficient conversion and integrated technological solutions.

The natural fibrous mineral serpentinite and waste generated can be considered as a potential source of producing sorption-filtering materials. Specifically, serpentinite consists mainly of serpentine group minerals with admixture of carbonates, amphiboles, talc, ore minerals magnetite, and chromite, with composition described by the general formula $Mg_3Si_2O_5(OH)_4$. The fibrous variety of serpentine, known as chrysotile asbestos, is widely used in chemical industry for obtaining high-purity magnesium and silicon oxides, heat-resistant ceramics, refractories, and adsorbent (Lv *et al.*, 2020; Yerdos *et al.*, 2019; Zakaria *et al.*, 2019; Lee, Jo, and Ryoo, 2017; Zhang *et al.*, 2017; Baigenzhenov *et al.*, 2015; Jo *et al.*, 2013).

Based on the background above, this study aimed to develop and create new zeolite chemical adsorbent using technogenic waste of asbestos production for purification of heavy hydrocarbon feedstock. The novelty of this study lies in the high-temperature synthesis of zeolite chemical adsorbent using technogenic waste of asbestos production containing SiO_2 , as the main mass, nickel sulfate ($NiSO_4 \cdot 7H_2O$), and molybdenum oxychloride ($MoOCl_2$) for demetallization and desulfurization of heavy oil feedstock.

In previous studies by Ongarbayev *et al.* (2019), demetallization and desulfurization of heavy vacuum fraction were carried out in the presence of zeolites adsorbent containing vanadium oxide xerogel at a temperature of 613 K, pressure 1 atm, and volumetric feed rate 1 h. The results showed a significant decrease in vanadium, nickel, and iron content by 90, 70, and 60%, respectively, along with a reduction in sulfur content from 1.97 to 1.36%.

2. Methods

2.1. Materials

The activity of chemical adsorbent used in this study depends on the rate of formation and transformation of surface intermediates. This process is determined by the nature of the interaction, including bond breaking through spatial configuration. The basic principle of activation is that the material is subjected to thermal treatment under appropriate conditions, inducing the formation of numerous pores, gaps, and cracks to increase the surface area of pores per unit mass. In engineering applications, both chemical and vapor-

gas methods of material activation are widely used. Therefore, the initial materials used in this study for the charge preparation and production of the active chemical adsorbent include asbestos waste (AW) obtained after hydrochloric acid leaching provided by KostanayMinerals (Republic of Kazakhstan). Chemical composition of the asbestos waste is presented in Table 1, with particle size of the material being $-2.0 + 1.0$ mm.

Table 1 Chemical composition of AW after leaching

Component	Chemical formula	Content, % wt.
Silicon oxide	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	90.0
Magnesium oxide	MgO	6.5
Iron oxide	Fe_2O_3	2.5
Remaining impurities	-	1.0

- calcium carbonate CaCO_3 , 99-99.9%,). – Sigmatec;
- sodium carbonate ("chemically pure" 99.8%) – Sigmatec;
- liquid glass, diluted to 10 % – Sigmatec.

2.2. Mixing

Asbestos waste from hydrochloric acid leaching was obtained using the method of (Shayakhmetova *et al.*, 2019). The procedure for the preparation of mixed adsorbent is similar to ceramic production applications. This includes initial components preparation, grinding, followed by mixing and wetting, pellet molding, hardening, and calcination. Grinding of the initial components is essential, ensuring that the material dispersion is suitable for the process adopted and meets the requirements for the properties of adsorbent. The active adsorbent was prepared by adding soluble salts of nickel and molybdenum as semi-hydrous nickel sulfate and ammonium paramolybdate to the base material, namely serpentine after leaching and calcium carbonate. The weight ratio of the materials to be added and the active ingredient in mixed catalysts are given below:

Table 2 Composition of synthetic chemical adsorbent

Name of a compound	The formula	Content, %
Serpentine after leaching	SiO_2	38.0
Calcium carbonate	CaCO_3	44.0
Baking soda	Na_2CO_3	5.0
Nickel sulphate	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	3.0
Ammonium paramolybdate	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 7\text{H}_2\text{O}$	10.0
Total		100.0

As shown in Table 2, the mixing of charge components and grinding to achieve a homogeneous mass composition was carried out for 10 minutes in the dry state using a grinder to reduce the particle size to less than 100 microns. Subsequently, plasticizers in the form of sugar molasses (0.5% of the total mass), and sodium lignosulphonate (2.0%) were added to the mixture. Plastic molding with the addition of water was carried out and the molded materials obtained were subjected to a two-stage firing at 923 K for 60 minutes to form wollastonitic structure and 1323 K for 30 minutes. Consequently, this processing led to the formation of the synthetic adsorbent with wollastonite structure.

2.3. Test

The following equipment was used to determine the mineralogical composition, chemical composition, and formation structure of the synthetic chemical adsorbent obtained with various activator additives. Specifically, X-ray data were obtained using a BRUKER D8 ADVANCE machine. X-ray fluorescence analysis was performed on a Venus 200 PANalytical B.V. (Holland) spectrometer with wave dispersion. Chemical analysis of samples

was performed on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, PerkinElmer). Mapping of elemental and phase composition of samples was carried out on electron-probe analyzer JXA-8230 by JEOL (Japan). Thermal analysis was performed using Jupiter STA 449 F3 synchronous thermal analysis unit and the results were processed with NETZSCH Proteus software. To determine the value of the total specific surface of meso- and macroporous substances and materials, the SORBTOMETR-M device was used by the method of thermal desorption of gas-adsorbate - BET method based on the Brunauer-Emmett-Teller equation. The specific surface area measurement range is 0.3-2000 m²/g, with a temperature of 323-573 K.

3. Results and Discussion

3.1. Study of temperature regimes (thermal analysis) to produce synthetic chemical adsorbent

The prepared mixture was thermally heated to 1273 K with an exposure time of 1 hour to determine the decomposition products of calcium carbonate and secondary calcium silicates. The analysis was carried out using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) on a Q-1000D derivatograph. When the sample was dynamically heated from 293 to 1273 K, a series of thermal peaks were observed on the DTA curve. Among these peaks, 413, 873, and 1093 K were identified as endothermic, formed by the release of hydroxyl and carbon dioxide water molecules into the atmosphere. The formation of the fourth peak at 998 K was due to the exothermic destruction of the hydro-silicate, which caused an influx of thermal energy into the system, as shown in Figure 1.

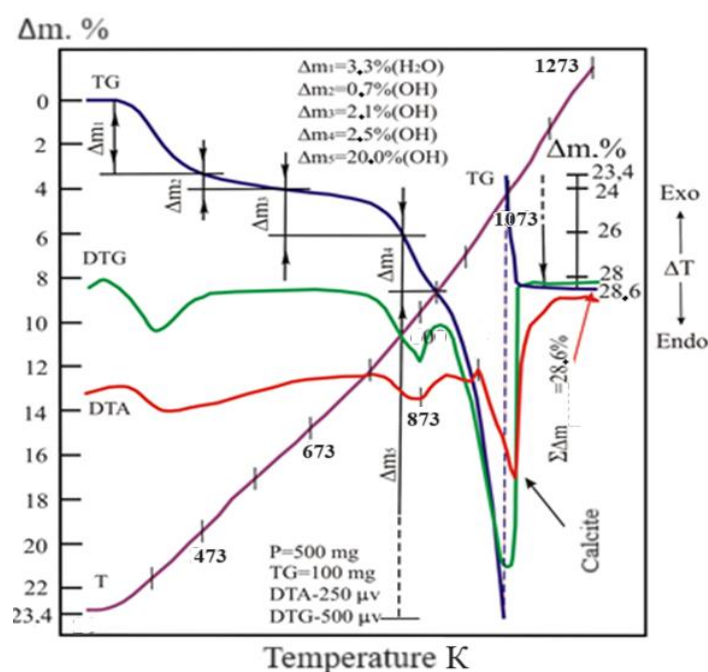


Figure 1 TGA of the sample

The morphology of the DTA-curve in the interval of 623 - 1003 K was similar to the differential curve of serpentine decomposition. Based on the configurations of TG and DTG lines, the low intensity of dehydration of sample components and the weak similarity of trajectories of thermal peaks concerning the peaks of classical serpentine can be traced. This discrepancy showed that the structure of the supposed mineral was found to be very defective, and unable to fully meet the crystalloid-chemical requirements of the reference

serpentine. Therefore, the composition of the sample was determined using the amount of constitutional water (OH), corresponding to the sum of weight loss $\Delta m_3/2 + \Delta m_4 = 1.05\% + 2.5\%$, which is the addition of second part Δm_3 and the whole part Δm_4 , as shown in Table 3. Considering the stoichiometric formula of serpentine, the amount of this mineral in the composition of the sample was found to be 24.6%.

Table 3 Thermogravimetric readings of the test sample between 293-1273 K

The sequence of weightloss	Weight loss (%)	Volatile components of the heated sample	Decomposition stages (K)
Δm_1	3.3	H ₂ O	293 - 473
Δm_2	0.7	OH	473 - 623
Δm_3	1.05	OH+CO ₂	623 - 833
Δm_4	2.5	OH	833 - 913
Δm_5	22.5	CO ₂	913 - 1273
$\Sigma \Delta m_{1273K}$	28.6	H ₂ O, OH, CO ₂	293 - 1273

The other component encountered in the sample tested is calcite, detected by the strong emission of carbon dioxide into the atmosphere. The removal of calcite from the system occurs at the high temperature, forming a plumb line of weight loss on the TG curve. In contrast, on the DTG-curve, the release of carbon dioxide from the system formed a very deep peak at 1073 K, showing a high dissociation rate. Consequently, the DTA curve showed an intensive peak from 1093 K, indicating a substantial outflow of thermal energy from the sample as presented in Figure 1. The thermal degradation pattern observed for CaCO₃ corresponded with well-oxidized calcite.

According to the amount of CO₂ emission (1.05% + 22.5%) shown in Table 3 and the stoichiometric formula, the content in the sample was found to be 53.5%. Meanwhile, the 3.3% of water ejected from the sample at 293 – 473 K was not part of the serpentine and calcite, leading to the classification as mechanically bound water of impurity status. This showed that di-calcium silicate Ca₂SiO₄ was formed at 773 K, while tri-calcium silicate Ca₃Si₂O₇ and wollastonite CaSiO₃ began at 1123 K. Based on these results, it can be concluded that Ca₂SiO₄ and Ca₃Si₂O₇ are unstable intermediate compounds. According to these thermograms, the formation of wollastonite commenced when Ca₃Si₂O₇ formed at temperatures above 1173 K. The formation of the mineral wollastonite occurred at high temperatures with the release of carbon dioxide, as expressed by chemical equation 1, indicated by the thermodynamic data of chemical reaction presented in Table 4:



Table 4 Thermodynamics of the wollastonite formation reaction

T (K)	deltaH (kJ)	deltaS (J/K)	deltaG (kJ)	Log (K)
273	89.135	162.947	44.627	-8.535
473.0	87.550	158.744	12.441	-1.374
673.0	84.903	154.135	-18.853	1.463
873.0	80.404	148.380	-49.154	2.941
1073.0	77.377	145.263	-78.513	3.822
1173.0	73.652	141.875	-92.788	4.132
1273.0	71.827	140.382	-106.901	4.386
1373.0	69.907	138.931	-120.866	4.598

Based on the thermal analysis and thermodynamic reactions, the formation of synthetic chemical adsorbent in the form of mineral wollastonite occurred at 1173-1373 K.

3.2. X-ray phase and analyses of samples

X-ray diffraction analysis of synthetic chemical adsorbent in Figure 2 and Table 5 showed the formation of new mineral. Specifically, pavellite (CaMoO_4) crystallized in tetragonal syngony was identified, forming dipyramidal and tabular crystals, which showed a density of 4.25 - 4.52 g/cm^3 , with 72% MoO_2 and 10% Mo composition. Libenbergite (Ni_2SiO_4) was detected, characterized by fine pyramidal crystals, grains crystallized in rhombic syngony, and a density of 4.50 - 4.60 g/cm^3 , containing 56% nickel.

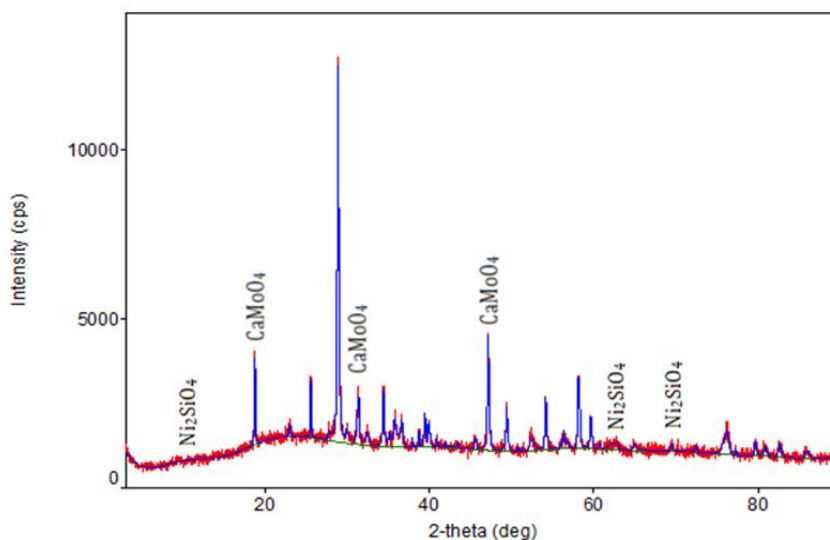


Figure 2 Diffractogram of the obtained synthetic chemical adsorbent

Table 5 Results of semi-quantitative analysis of crystalline phases

Phase name	Formula	SemiQuant [%]
Wollastonite	CaSiO_3	85.0
Powellite, syn	CaMoO_4	6.0
liebenbergite, high, syn	Ni_2SiO_4	2.0
Silicon Oxide	SiO_2	7.0

The XRD data showed that the high-temperature synthesis produced a well-formulated synthetic material, with wollastonite CaSiO_3 constituting 80 - 85% of the main mineral composition. The integration of activators in the form of molybdenum oxychloride (MoOCl_2) and nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) promoted the formation of new minerals in the form of powellite (CaMoO_4) and libenbergite (Ni_2SiO_4), which are fully synthesized based on free calcium and silicon compounds. The presence of these compounds did not impair the physicochemical properties of the synthesized material but promoted the formation of a porous structure due to its small density and specific surface area. The resulting product also contained free amorphous silica in the form of cristoballite, constituting 7% of the composition.

3.3. BET method

In selecting adsorbent for a particular practical application, information about porous structure is essential. For appropriate selection, there is a need to know whether the inherent pore radius distribution corresponds to the molecular sizes of given sorbates and ensures rapid penetration of substances deep into sorbent granules.

Adsorption potential in micropores is significant due to the superposition from neighboring walls. Therefore, molecules capable of penetrating micropores show significantly higher adsorption affinity compared to those fixed in meso- or macropores. To

determine the specific surface area and pore radius distribution of porous bodies, the BET method was applied using SORBTOMETR-M device, as shown in Table 6.

As shown in Table 6, the values of the specific surface area and pore volume of the obtained active component are small. Moreover, micropores are important for the activity of material and demetallization process due to their diameters of approximately 2 nm, which corresponds to the size of the adsorbing molecules. The presence of micropores also facilitates the development of the main part of the inner surface of the active component, positively influencing the properties of the synthetic chemical adsorbent.

Table 6 Specific surface area, specific volume, and average pore size of materials

Sample	Specific surface area, m ² /g	Specific pore volume, cm ³	Average pore size, Å	Weight, g
Obtained chemical adsorbent	4.0-6.0	0.137	1.714	0.1345

3.4. Cleaning of heavy crude oil from metal impurities

The destructive-adsorptive thermal contact process of demetallization consists of short-term contact of oil feedstock with adsorbent in the two-section reactor heated at temperatures of 573 - 723 K. Due to the contact between the feedstock and the hot adsorbent, hydrocarbon vapors are formed, which are mixed with water vapor and transported to the gas venting line, as shown in Figure 3.

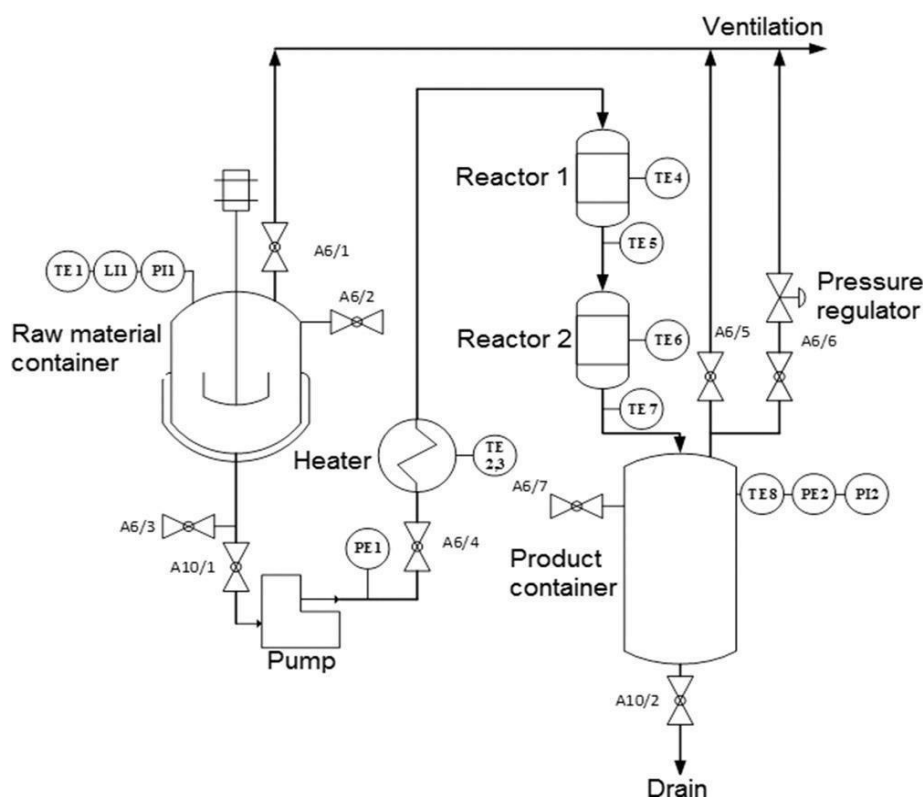


Figure 3 Process flow diagram for demetallization and desulfurization of heavy oil residue

Testing was carried out using tar obtained from the delayed coking unit of "Pavlodar petrochemical plant" LLP, a viscous slow-moving liquid with a mass fraction of water of approximately 0.1 wt.%. This tar contains metals, such as vanadium 400-600.0 mkg/kg, nickel 50 - 70.0 mkg/kg, iron 30 - 70.0 mkg/kg, the mass fraction of sulfur 2.5 - 3.5%, ash content -0.02 wt. %, coking - 18 wt. %, density at 273K - 1000.0 kg/m³, the boiling point -

653 K. Furthermore, testing of demetallization of heavy oil residue was carried out at temperature zone of 593 - 693 K, contact time of 60 minutes, and the pressure was kept within 8 - 10 atm. The results obtained were presented in Table 7, where the optimum temperature zone of heavy oil demetallization was found to be 673 - 683 K. However, the tar commenced to boil and coke due to an increase in temperature above 683 K, which adversely affected demetallization process. This phenomenon also affected the content of vanadium, nickel, iron, and sulfur in vacuum residue, which decreased from 540 to 52 mkg/kg, 50 to 26 mkg/kg, 50 to 12 mkg/kg, and 3.50 % to 2.39 %, respectively. The maximum degree of extraction at these metals was found to be 90.37%, 48.0%, 76.0%, and 31.7%, respectively.

Table 7 Metal and sulfur content of tar before and after testing as a function of process temperature

Raw material type of adsorbent	and T, K	Element content			
		V, µg/kg	Ni, µg/kg	Fe, µg/kg	S, %
Initial tar	-	540.0	50.0	50.0	3.50
Tar after contact with modified chemical adsorbent	593	500.0	50.0	50.0	2.65
	613	488.0	50.0	50.0	2.61
	633	450.0	43.0	40.0	2.58
	653	330.0	35.0	33.0	2.53
	673	70.0	31.0	21.0	2.45
	683	52.0	26.0	12.0	2.39
	693	23.0	22.0	7.0	1.50

4. Conclusions

In conclusion, this study showed the developmental processes for dehydrating and obtaining active components to create a matrix base of synthetic chemical adsorbent from composite materials using chrysotile asbestos production waste. The adsorption properties of obtained composite catalysts were practically investigated. The results showed that the optimal temperature zone for demetallization of heavy oil residue was 653-683 K, with a contact time of 60 minutes and a pressure of 8-10 atm. Under these conditions, a significant decrease was observed in the content of vanadium, nickel, iron, and sulfur from 540 to 52 mkg/kg, 50 to 26 mkg/kg, 50 to 12 mkg/kg, and 3.50% to 2.39%, respectively.

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