Enrichment of mineral raw materials: selection of local clay minerals for the purpose of obtaining adsorbents for purification of petroleum products

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Abstract. Geotechnologies and subsoil use play a key role in the rational development of the mineral resource complex, requiring innovative approaches to the enrichment of mineral raw materials. This article discusses a promising direction in the beneficiation of mineral raw materials, focused on obtaining adsorbents from local clay minerals for the effective purification of petroleum products and environmental protection. The article presents a study on the potential of local clay minerals to create effective adsorbents using a mechanochemical activator. The study includes a review of the chemical and mineralogical composition of clays collected in the region, as well as their particle size distribution and differential thermal analysis.

1 Introduction

Petroleum products, such as paraffins, are important raw materials for various industries, including medicine, cosmetology, food processing and paper production. However, before these petroleum products can be used in high-tech and sensitive applications, they must be ensured to be as pure a*s possible. In this context, purification with clay adsorbents or adsorbents of plant origin becomes a key stage of production [1].

Clays, as natural minerals, have unique adsorption properties that can capture and remove contaminants from petroleum products. The use of clay adsorbents to purify paraffins from impurities and heavy hydrocarbons allows us to obtain not only a purer product, but also ensures that it meets high quality standards.

The use of local clay mineral adsorbents offers promising opportunities in this area. One promising approach is the use of local clay minerals using a mechanochemical activator [2, 3].

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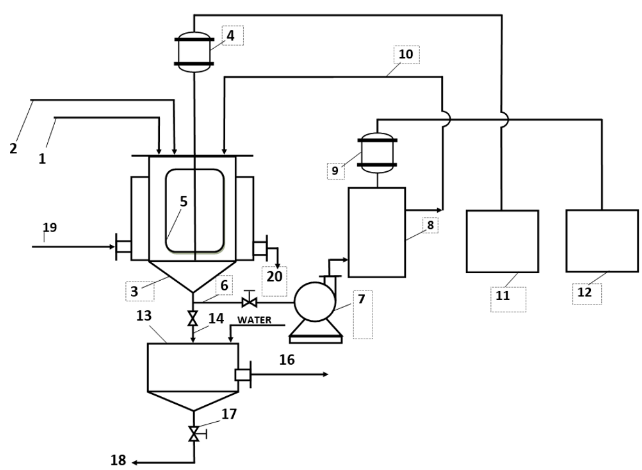
2 Materials and methods

Clay minerals have unique properties that make them potentially valuable materials for creating adsorbents. However, to maximize their adsorption characteristics, it is necessary to develop effective processing methods. For example, acid activation of bentonite and palygorskite clays using microwave radiation. It was found that the microwave activation of bentonite leads to the destruction of the structure, the expansion of the surface and a change in the structure of the pores, which affects the textural characteristics. To activate local bentonites and palygorskite, it is recommended to choose solutions of inorganic acids in accordance with their mineralogical and chemical composition. At the same time, the use of volumetric heating of clays, for example, microwave radiation, enhances the activation process and increases the volume of micro-, macro- and transient pores of the adsorbent compared with traditional convective heating. [4] With the same perspective, the method of acid activation of minerals using a mechanochemical activator is used. A mechanical-chemical activator is a promising tool for improving the structure and increasing the activity of clay materials. Figure 1 below shows a scheme of an installation for acid activation of clay adsorbents using a mechanochemical activator.



1- clay supply line;2-acid supply line ;3-mixer ;4,9-motor; 5-agitator ;6-suspension discharge line ;7-pump ;8- mechanochemical activator ;10-suspension circulation line ;11,12-control unit ;13-filter sump ;14-line for the supply of activated clay ;15-water supply line ;16-filtered clay drainage line ;17-valve ;18- line for draining acidic water into the sewer ;19-hot water supply line ;20-condensate drainage line.

Fig. 1. Scheme of a laboratory installation for acid activation of clay adsorbents using a mechanochemical activator.

This installation functions as follows: through line 1, the activated clay enters the mixer 3, where a 20% aqueous solution of sulfuric acid (H2SO4) is supplied through line 2. Mixing of the suspension in the mixer 3 is carried out using the motor 4 of the agitator 5. From the mixer 3, the suspension is sent along line 6 using a pump 7 to a mechanochemical activator (MHA) 8, from where it returns to the mixer 3 via line 10. The engines 4 and 9 are controlled using the control units CU-1 and CU-2, respectively. The mechanochemical activator consists of a stator housing with a rotor mounted in it on the horizontal axis, which is made in the form of a set of conical roller elements. Activated clay along line 14 from the cone part of the mixer 3 enters the filter sump13, from where the acidic water along lines 17 and 18 is sent to the sewer. . The remaining clay in the filter 13 is washed with water (condensate) coming through the line 15. From filter 13, clay is sent along line 16 for drying and grinding. The temperature in the mixer 3 is maintained by hot water coming through line 19, where condensate is discharged through line 20. The use of this installation in the production of activated clay adsorbents has shown its operability and reliability during operation. At high mixing speeds, the suspension reduces the activation time by 2-3 hours and increases the porosity of the resulting clay adsorbents.

In clay deposits, mixtures of minerals with other non-clay substances (mineral salts, metal oxides, etc.) are mined. Therefore, the selection of clay minerals for the production of adsorbents requires knowledge of the content of harmful substances removed from paraffin and ceresin, their sorption characteristics, etc.

As a literature review has shown, to obtain clay adsorbents for the purification of liquid hydrocarbons, mineral oils, paraffins and ceresins, bentonites, palygorskites, opoka-like and hydromica clays, which are available in sufficient quantities in Uzbekistan, are widely used [5,6,7,8].

The process of producing adsorbents involves grinding clay minerals, activating them and modifying them to increase their ability to adsorb petroleum products.

When selecting clays for the production of adsorbents, the main indicators are their mineralogical and chemical compositions, which differ greatly from each other.

To obtain clay adsorbents, montmorillonite minerals and then apapulgites, opoka, palygorskites, etc. are most often used. The structural structure of these minerals is different and therefore the pores and diameters formed in them also differ from each other.

3 Results and discussion

In some regions of Uzbekistan there are valuable clay minerals that can be used as raw materials for the production of adsorbents. For example, in the Fergana region there is hydromica clay from the Shursui deposit and palygorskite from the Tul-Sokh deposit. We studied the chemical composition of these clays, the results of which are presented in Table 1.

Table 1. Chemical composition of clays from the Fergana region of Uzbekistan, selected for the production of adsorbents.

Clay deposit name	Chemical composition of selected clays, % of absolutely dry matter											
	SiO_2	TiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_3	SO_3	Fe_2O	other impurities	Sum
Shorsui hydromica clay (SHC)	58.75	0.91	18.09	5.7	2.97	0.39	2.05	0.52	0.05	8.95	15.72	99.83
Tul-Sokh palygorskite	46.79	-	8.63	2.74	10.08	-	1.6	1.99	-	3.41	24.33	99.75

The particle size distribution is considered one of the important parameters of clays treated with aqueous solutions of acids. The original bentonites, palygorskites, hydromica and opoka-like clays have different particle sizes, which is detected by the Sabanin-Robinson sedimentation method [9].

Of equal importance is differential thermal analysis (DTA) of the initial clays selected for the production of adsorbents. We performed this analysis on a Kurnakov FPK-55 pyrometer with a temperature change rate of 30 0C/min.

Table 2 presents the results of the above analyzes of selected clays.

Table 2. Indicators of granulometric composition and differential thermal analysis of selected clays.

Name of clay deposits	Granulometric composition of clays, %		Temperature effect DTA, 0C		
	Residue on sieve with mesh 02 K	Residue on sieve with mesh 0063	First	Second	Third
Shorsui hydromica clay (SHC)	1.1	98.9	180-230	480-650	810-870
Tul-Sokh palygorskite (TSP)	2.2	97.8	250-300	650-750	900-950

From Table 2 it can be seen that the selected local clays are close to each other in granulometric composition, and their differential thermal analysis (DTA) shows significant differences in the temperature “effects” between them, which must be taken into account when selecting the temperature of their activation and drying.

Sedimentation analysis of selected clays for the production of adsorbents showed that, in terms of their granulometric composition, they belong to finely dispersed raw materials.

Table 3 presents the results of analyzes of the dispersed composition and specific surface area of selected local clays.

Table 3. Disperse composition and specific surface area of selected local clays.

Name of clay deposits	Content of fractions, %			Specific surface area, *103, m2/kg
	less than 0.01 mm	less than 0.1 mm	less than 1.0 mm	
Shorsui hydromica clay (SHC)	82.7	16.2	1.1	295
Tul-Sokh palygorskite (TSP)	76.5	21.4	2.1	286

From Table 3 it can be seen that high dispersion is observed in the Shorsu hydromica clay (fractions with a size of less than 0.01 mm are 82.7%, and the specific surface area is greater in the Tul-Sokh palygorskite (286 * 103 m2/kg).

It is known that the amount of bound water can be used to judge the degree of hydrophilicity of selected local clays. We studied this indicator for selected local clays, the results of which are presented in Table 4.

Table 4. Hydrophilicity indicators of selected local clays.

Name of clay deposits	Heat of wetting of clay (Q), cal/g	Amount of bound water in clay (B), %
Shorsui hydromica clay (SHC)	23.8	30.74
Tul-Sokh palygorskite (TSP)	19.7	26.15

From the table 4 shows that the heat of wetting and the amount of bound water in the Shorsu hydromica clay is greater than in the Tul-Sokh palygorskite, which is very important to know when activating and drying them.

Traditionally, clay minerals are activated with 15-25% solutions of sulfuric acid, hydrochloric acid, etc. acids, for 6-8 hours of mixing the mixture at speeds up to 150 rpm under draft or vacuum. This activation of clays is not effective enough because in this case, the solid structure of the resulting adsorbent is severely destroyed, transition (transport) and internal pores do not open, which negatively affects its sorption activity.

Taking this into account, recently more and more attention has been paid to the use of unconventional methods of activating clay minerals: the use of magnetized solutions, microwave radiation, ultrasonic influence, etc.

In contrast to the above, mechanochemical activation (MCA) of clay minerals using solutions of inorganic acids is carried out under intense mechanical and chemical influence on their mixtures (speeds of more than 1000 rpm).

Over the last decade, the mechano-chemical method has undergone rapid development in many areas of chemical technology, and mechanical chemical agents of varying power and productivity have been created and implemented. Leaching of individual compounds from clay minerals using various solutions of inorganic acids and MCA is a very complex and insufficiently studied process, which is associated with the composition of activated clays, the design of MCA, etc.

Mechanical action on a solid is usually a combination of pressure and shear. Here it is important to determine the role of each in changing the physicochemical properties of a solid substance (for example, clay). Studies of the behavior of solids under pressure are not only necessary for understanding the mechanisms of mechanochemical processes, but are also very promising as one of the powerful methods for studying structural and intermolecular interactions. Even more important are studies of the combined influence of pressure and shear deformation of a solid. MCA in mills is the most common leaching method in chemical technology. Its main parameter for regulating the MCA process is the gap between the rotating bodies and their speed, achieved in a few seconds of change.

We conducted a series of experiments to study the effect of MCA on the adsorption properties of selected local clays. At the same time, a 15% aqueous solution of hydrochloric acid (HCl) was used for the leaching of Tul-Sokh palygorskite (TSP), and 20% sulfuric acid (H2S04) was used for Shorsui hydromica clay (SHC) at a temperature of 50-60 0C. Moreover, the gap between the rotating MCA elements was maintained at 1-1.5 mm, and the engine speed was changed from 500 to 2000 rpm.

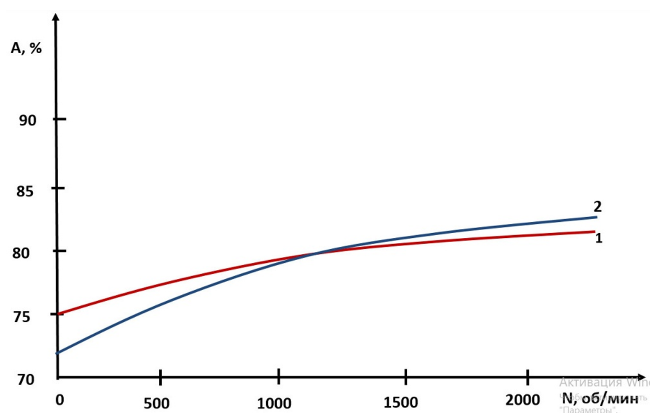


Fig. 2. The change in the sorption activity of local clays depending of MCA rotations for: 1- Tul-Sokh palygorskite (TSP); 2- Shorsui hydromica clay (SHC).

Figure 2 shows the results of a study of the effect of MCA rotations on changes in the sorption activity of local clays during their leaching at 50-60 0C.

Figure 2 demonstrates that with an increase in the number of revolutions of MCA to 1500 rpm, the sorption activity of selected clays increases and then gradually stabilizes.

The temperature of the MCA of clays strongly changes the sorption activity of the adsorbents obtained, which is associated with a decrease in the viscosity of the acid solution used and an acceleration of the reaction of its interaction with oxides of clay minerals. Therefore, determining the temperature optimum for the MCA of local clays is considered an urgent task.

We have studied the effect of MCA temperature on the sorption activity of the obtained clay adsorbents.

Figure 3 shows the changes in the sorption activity of local clays depending on the temperature of the MCA.

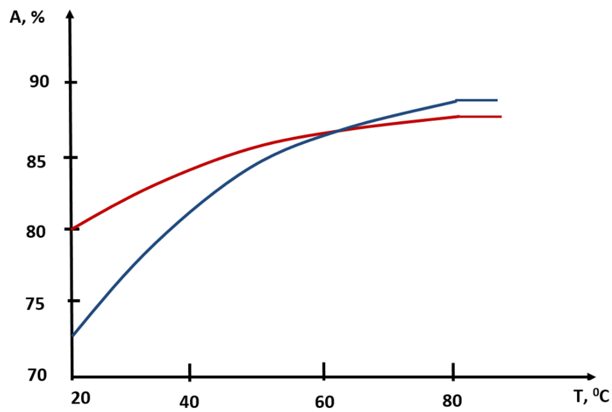


Fig. 3. The change in the sorption activity of local clays depending of MCA temperature for: 1- Tul-Sokh palygorskite (TSP); 2- Shorsui hydromica clay (SHC).

Figure 3 shows that with an increase in the temperature of MCA to 80^{0}C, the sorption activity of clays increases greatly and then begins to stabilize.

4 Conclusion

Thus, experiments conducted to assess the influence of technological parameters of MCA have shown that local clays have good sorption properties. The revealed differences between local clays are a consequence of their peculiar mineralogical and chemical composition.

Moreover, the use of an unconventional MCA method instead of conventional mixing allowed to increase the sorption activity of the adsorbents obtained by 1.3-1.5 times, and the use of 15% hydrochloric acid during leaching of local clays rich in CaO (TSP) allowed to reduce gypsum formation by 50-75%, which is very important when obtaining active adsorbents.

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