THE USE OF NATURAL FILTRATION SORBENTS TO SOLVE THE SAFETY PROBLEMS OF INDUSTRIAL POLLUTION FACILITIES

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Abstract

This work is devoted to the review of mineral and organic natural sorbents for the purpose of purification of polluted waters of industrial enterprises. Structural features, differences in the composition and properties of the most common natural sorbents, features of their application and sorption mechanisms of pollutants are shown. The main mechanisms of sorption for clay minerals and zeolite is ion exchange; for siliceous rocks such as diatomite, tripoli and gaize - physical adsorption on the surface of pores and reaction with silonol groups. Organic natural sorbents have both mechanisms of complex formation and physical adsorption, as well as ion exchange. It is shown that the creation of multicomponent granular permeable granules can significantly increase the efficiency of natural sorbents and will make their use more accessible and improve the safety of the industrial sector and nuclear legacy facilities.

Keywords: sorption, sorbents, glauconite, zeolite, diatomite, vermiculate, coal, peat

I. Introduction

One of the most important issues related to the industrial and petrochemical complex, as well as nuclear energy is to ensure the safety of man-made pollution and nuclear legacy facilities. As a result of the development of industry, several million tons of waste of varying degrees of danger are produced annually. Many specialists in various fields have been involved in the problem of solving such safety issues, however, work on the development of barrier compositions is still fragmented and unsystematic. The main problem of modern industrial water treatment is that the technologies used have a number of limitations, the main of which is the need to build an entire purification complex, with its own infrastructure, expensive equipment and consumables. In most cases, the available technologies are designed for selective sorption, the need to use several types of water treatment at once, and a high consumption of energy and reagents. Moreover, these systems are generally only suitable for controlled wastewater treatment and are not suitable for ground and surface water, as well as underlayment and bridging barrier elements in near-surface landfills.

The aims and objectives of this work is to study summarize the obtained data on sorption and operational properties of mineral and organic natural sorbents for the purpose of purification of polluted waters of various industrial enterprises. The advantage of these composites is the low cost and availability of raw materials for their production, high efficiency, ease of operation, no need for capital expenditures for the construction of an industrial cleaning complex, as well as scalability - the ability to use both mobile and stationary cleaning complex.

II. Methods

This work has been prepared on the basis of materials obtained as a result of geological, mineralogical and physicochemical works, as well as an analysis of previously published literature on this topic. Experiments on sorption, desorption, as well as the study of operational properties were carried out on natural and modified rocks of various deposits in Russia: Yagodninskoe and Khotynets zeolite deposits (Kamchatka Territory and Orel Region, respectively), Inzenskoe diatomite deposit (Ulyanovsk Region), Potaninskoe vermiculite deposit (Chelyabinsk oblast), the Karinskoe deposit of glauconite (Chelyabinsk oblast), the peat deposits of raised bogs (Tver oblast), Chernogorsk hard coal deposit (Rep. Khakassia), Pavlovsk brown coal deposit (Primorsky Krai).

III. Results

Natural sorbents include rocks and minerals formed in the natural geological environment, the structural features of which give them increased sorption properties. Mineral sorbents include quite a list of minerals that mainly have various structural defects, and as a result, the presence of an uncompensated negative charge in the structure of the mineral. Such natural sorbents have a high cation exchange capacity with respect to various metal cations and organic compounds. This group mainly includes clay minerals (smectia, illite, glauconite, vermiculite, etc.) and zeolites (clinoptillolite, mordenite, chabazite, etc.) (Fig.1) [1, 2].

Smectite minerals, are the basic components of bentonite clays. They are a class of layered aluminosilicates with two tetrahedral sheets and one octahedral sheet. Due to isomorphic substitutions in octahedral and tetrahedral sheets, the whole layer acquires a negative charge, which is compensated by interlayer cations thus resulting in the high sorption properties typical of smectite minerals [1]. Since smectite is a highly swelling mineral, it is mainly used as hydraulic seals and safety buffers, for example, in the deep disposal of radioactive waste or the creation of overlapping screens. Smectites are not used as a filtration sorbent.

Vermiculite is also layered aluminosilicates with two tetrahedral sheets and one octahedral sheet. However, unlike smectite, vermiculite does not swell on contact with water and has a lower cation exchange capacity. A distinctive feature of vermiculite is significant expansion when heated.

Illite is one of the most common micaceous minerals, however, it does not form commercial deposits by itself and is mainly found as an admixture with other clay minerals. Its ferruginous variety is glauconite, which is characterized by a globular shape of the structure of aggregates and widely distribution [3]. Interlayer-deficient micas have a layer structure similar to smectite (2:1), however, their characteristic feature is the presence of a strongly bonded potassium cation in the interlayer space and a high layer charge [1].

Zeolites, also known as molecular sieves for their specific structure and properties, are hydrated framework aluminosilicates with intracrystalline channels and cavities. Due to the isomorphous substitution of Al for Si, the negative charge is formed in the channels, which requires compensation by cations causing a high selectivity for zeolites to a number of substances including radionuclides [1, 4]. Zeolite is one of the most demanded natural materials for the sorption of heavy metals and radionuclides [5].

Diatomites are siliceous rocks consisting of remnants of diatomaceous algae possessing high specific surface area due to their very fine average particle size and therefore micro- and macroporosity [1, 6]. Natural and modified forms of diatomite have been used for the removal of organic compounds, oil spills, heavy metals and radionuclides from liquid waste [7].

Fig. 1: *Photographs of natural mineral sorbents: a – vermiculite, b – glauconite, c – zeolite, d – diatomite.*

Natural hard and brown coal, as well as peat, can be categorized as organic sorbents (Fig. 2). Coal, a flammable mineral, predominantly comprises organic matter that has undergone lithification through temperature and pressure. Its utilization as a sorbent dates back to ancient times, due to its ability to absorb large quantities of water, its high porosity, and the presence of humic and humic acids [2].

High-moor peat is created in elevated moors and areas with excessive water content through the process of plant debris decomposition. Sphagnum mosses are the primary contributors to the formation of peat in these marshy environments [3]. Peat consists of plant remnants that possess a branched structure, with the outer surface being adorned with a consistent network of pores that measure 5-10 microns in diameter. The pores exhibit diverse shapes, including round, elongated, irregular, or papilla forms, as depicted (Figure 2) [2].

There are a fairly large number of works devoted to the study of the sorption properties of shungite, however, our own studies of the proportion of heavy metals and radionuclides showed that shungite itself does not participate in sorption processes, the main sorption falls on the minerals of the smectite and illite groups present in the rock as an impurity.

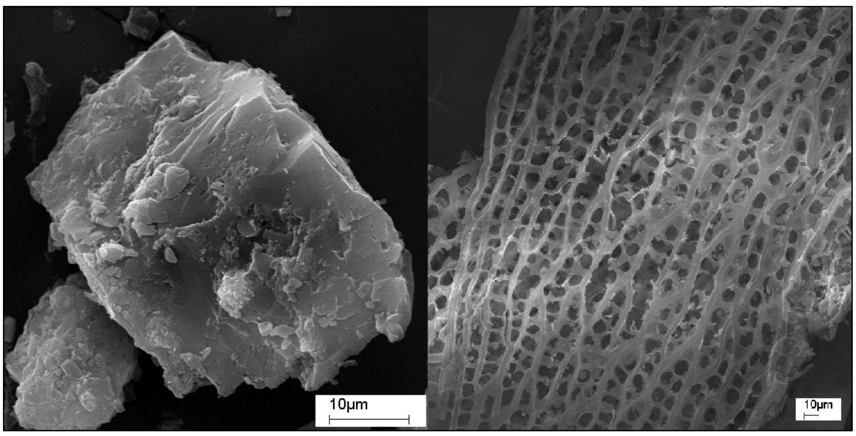

Fig. 2: *Scanning electron microscope images: hard coal (left), peat (right).*

As for the mechanisms of sorption, three main types can be distinguished: ion exchange, complex formation and physical adsorption. Each natural rock and mineral is characterized by one or another mechanism.

For example, for organic sorbents, a large specific surface area and the presence of macro and micropores, which are responsible for physical adsorption on the pore surface, often play a leading role. An example of such sorbents with an increased specific surface area is activated coal. Complex formation processes also play an important role in the sorption of cations on organic sorbents, and to a lesser extent, ion exchange [2].

For silicite rocks, consisting of amorphous silica – diatomite, tripoli and gaize, the main mechanism of sorption is physical adsorption on the pore surface, as well as the reaction with silonol groups (≡SiOH) groups [8].

Clay minerals and zeolites are mainly sorbed due to their ion-exchange properties. However, the mechanisms of sorption on clay minerals have not been fully explored. For a deeper understanding of these processes, modern computer modeling methods are used [6, 9]. It has been shown that sorption processes on illites or vermiculate can also occur on basal surfaces, the so-called FES (Frayed Edge Sites) [10].

An important role in sorption is played not only by the mechanism of sorption, but also by the nature of the pollutant, as well as the size of its atom or molecule. The most sensitive to size are the minerals of the zeolite group, since they have a certain size of the channels into which the pollutants must freely pass. As was shown in our the work [4], synthetic zeolite A-13X had a specific surface area and a cation exchange capacity many times greater than natural samples, however, due to the small size of the channel inlet window, it was characterized by reduced sorption to cesium and strontium radionuclides.

In addition to the sorption of heavy metals, radionuclides and water-soluble organic compounds from aqueous solutions, natural sorbents have shown their effectiveness in collecting hydrocarbon spills, both on the soil surface and on water. The advantage of using natural raw materials is their low cost and availability. For these purposes, highly porous sorbents with a low bulk density, such as diatomite, tripoli and gaize, are mainly used. However, the use of modified glauconite has recently gained popularity [11]. Due to the treatment of its surface with a hydrophobizing agent, glauconite globules acquire buoyancy and easily remove oil spills from the water surface (Fig. 3a). Also the options for imparting magnetic properties to glauconite (Fig. 3b), which makes it easy to collect waste material using electromagnetic installations, are considered.

Fig. 3: *Microphotos of modified glauconite: left – contact angle of wetting of hydrophobic glauconite for oil spill response; right – globules of glauconite coated with nanomagnetite*

However, despite the high efficiency of natural sorbents, often comparable to synthetic counterparts, and their low cost, the main disadvantage is low performance properties, namely, lack of stability, low filtration and mechanical strength. Due to the admixture of clay minerals, in particular smectite and kaolinite, the granules are blurred and destroyed and the inner surface of the filters is silted.

The solution to this problem can be the creation of a technology for obtaining a multicomponent granular permeable composite based on natural and modified sorbents. These composites will combine various sorption mechanisms (ion exchange, complex formation, physical adsorption) and also have mechanical strength and high performance properties.

As a result, a granulation technology was obtained with the addition of various binders, in particular with the use of aluminous (AC) and portland cement (PC) [12]. The resulting granules have high operational and sorption properties. Dynamic experiments on the sorption of Cs with a duration of 200 hours (more than 8 days) were carried out on the obtained samples of granules,. Sorption was carried out from the Moscow tap water with the composition: total salt content - 310-330 mg/dm3; total hardness - 3.6-3.8 mg-eq / dm3; pH=7.3-7.8. Before the start of the experiments, indicator amounts (~105 Bq/dm3) of the 137Cs radionuclide were added to the water and kept for 5 days. The obtained results show that when passing 1000 column volumes of tap water, high values of purification factors (500-1000 units) from 137Cs are observed. The filtering capacity of the layer remained constant during the entire filter cycle (more than 200 hours), which indicates the mechanical strength of the granules (Fig. 4a). The effectiveness of the obtained granules was also confirmed in the purification of water from copper ions (Fig. 4b).

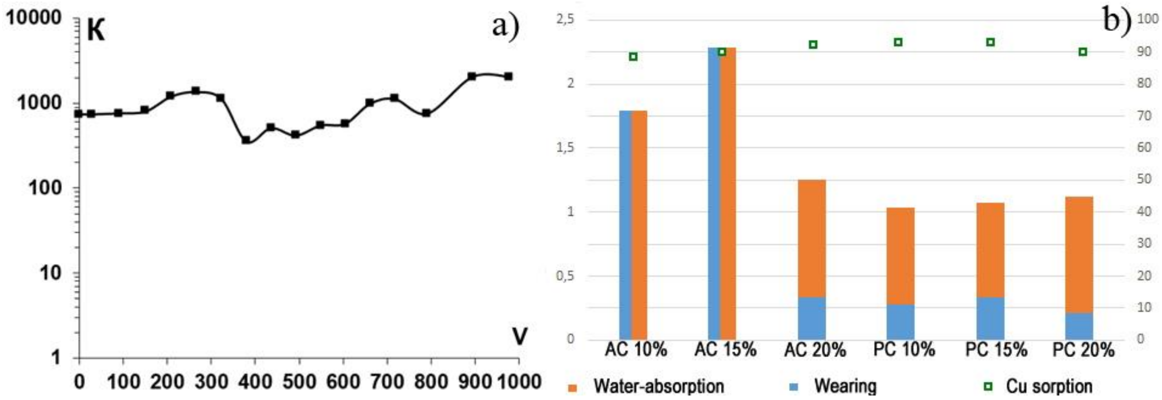

Fig. 4: *The experiments on granulated sorbents: a - output curve of sorption of 137Cs from tap water (K - the purification factor; V - the volume of filtrated solution), b - index of wearing, water-absorption and sorption of* Cu^{2+}.

IV. Conclusion

The use of natural sorbents at industrial facilities an urgent task, the solution of which will make it possible to create cheap and effective filtration or anti-migration systems for the purification of polluted waters from heavy metals, radionuclides, organic pollutants and oil products. Natural mineral-type sorbents include clayey rocks such as smectite, glauconite, vermiculite, siliceous rocks such as diatomite, tripoli and gaize, and zeolite rocks. Natural organic sorbents are mainly represented by hard and brown coal, as well as peat. However, the use of natural raw materials in their original form, with the exception of volcanogenic zeolites, is difficult, since natural granules have low strength and performance properties. The solution to this problem can be the development of a technology for obtaining multicomponent granular permeable granules. The development of new sorption composites and technologies for their application will make their use more accessible and improve the safety of the industrial sector and nuclear legacy facilities.

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