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THEORETICAL FOUNDATIONS OF ADSORPTION PROCESSES ON MODIFIED NATURAL ZEOLITES AND SORPTION OF AROMATIC HYDROCARBONS IN AQUEOUS AND GASEOUS MEDIA

Abstract. This article presents a theoretical analysis of the adsorption capacity of modified natural zeolites for the removal of aromatic hydrocarbons from aqueous and gaseous media.

The mechanism of the adsorption process is explained on the basis of physical and chemical adsorption theories, and the influence of the structural features and surface properties of zeolites on the process is investigated. Mathematical modeling of the adsorption process was carried out using Langmuir and Freundlich isotherm models, pseudo-first-order and pseudo-second-order kinetic models, as well as intraparticle diffusion and thermodynamic approaches.

The theoretical results indicate that thermally and acid-modified zeolites possess high potential for the effective sorption of benzo(a)pyrene (aromatic hydrocarbons) and can be considered promising adsorbents for environmental remediation technologies.

Keywords: adsorption, zeolite, benzo(a)pyrene, isotherm models, kinetics, thermodynamics.

Introduction. The rapid development of industry, energy production, and transportation sectors in modern times has led to a significant increase in anthropogenic impact on the environment. Aromatic and polycyclic aromatic hydrocarbons (PAHs), including benzo(a)pyrene (C20H12), are among the most hazardous pollutants from an environmental and sanitary perspective. Benzo(a)pyrene is characterized by high toxicity, mutagenic and carcinogenic effects, and belongs to the first hazard class.

This compound is mainly formed as a result of incomplete combustion of organic fuels (coal, fuel oil, diesel) and is emitted into the atmosphere with flue gases. In addition, the presence of benzo(a)pyrene and other PAHs is observed in industrial and domestic wastewater. Therefore, their effective removal from water and gas media remains an urgent scientific and practical problem.

Among existing purification methods, adsorption technology occupies a special place due to its simple operation, high efficiency, energy efficiency, and selectivity. The effectiveness of the adsorption process directly depends on the properties of the adsorbent used. In this regard, natural zeolites attract considerable interest as inexpensive, widely available mate-

rials with a porous structure.

1. Fundamental theory of adsorption processes

Adsorption is the process of accumulation of substances (adsorbate) on the surface or within the internal pores of a solid phase (adsorbent). The adsorption process consists of the following stages [1]:

- transport of the adsorbate from the bulk phase to the adsorbent surface;
- diffusion on the surface and within the pores;
- binding at adsorption sites.

According to the mechanism, adsorption is divided into two main types.

1.1. Physical adsorption

Physical adsorption occurs due to van der Waals forces. In this case:

- the process is reversible;
- the heat of adsorption is relatively low (5–40 kJ/mol);
- an increase in temperature weakens adsorption.

1.2. Chemical adsorption

Chemical adsorption is characterized by the formation of chemical bonds between the adsorbent surface and the adsorbate. In this case [2]:

- the heat of adsorption is high (40–800 kJ/mol);
- the process is often irreversible;
- high selectivity is observed.

2. Structure and surface properties of natural zeolites

Zeolites are crystalline aluminosilicate minerals and can be expressed by the general formula:

$$Mx/n[(AlO_2)x(SiO_2)y]\bullet mH_2O,$$

where M represents exchangeable cations (Na^+, K^+, Ca^{2+}, etc.), x and y are the numbers of Al and Si atoms, n is the cation valence, and mH_2O denotes crystalline water molecules.

The structure of zeolites consists of numerous micro- and mesopores, which ensures a large specific surface area. The negative surface charge mainly arises from the substitution of Si4+ ions by Al3+ ions.

However, natural zeolites mainly exhibit high sorption capacity toward cations and show relatively weak affinity for hydrophobic and anionic pollutants. To overcome this limitation, modification methods are applied [3].

3. Methods for zeolite modification (theoretical approach)

3.1. Thermal modification

Heating zeolites in the temperature range of 300–600 °C results in:

- removal of crystalline water;
- opening of pores;
- increase in specific surface area.

3.2. Acid modification

During acid treatment (e.g., H_2SO_4, HCl):

- partial removal of Al atoms from the structure (dealumination) occurs;

- the Si/Al ratio increases;

- pore diameter increases;

- hydrophobicity is enhanced.

These properties are favorable for the sorption of hydrophobic PAHs such as benzo(a)pyrene [4].

Theoretical interpretation of adsorption of aromatic hydrocarbons on zeolites

Aromatic hydrocarbons are hydrophobic, planar molecules and are mainly retained on the zeolite surface due to:

- π–π interactions;

- hydrophobic effects;

- physical entrapment within pores.

These interactions are more pronounced in acid-modified zeolites [5].

Conclusion

The theoretical analysis shows that modified natural zeolites are highly promising adsorbents for the removal of aromatic hydrocarbons from aqueous and gaseous media. The combined application of adsorption isotherms, kinetic, and thermodynamic models allows a deeper understanding of the process mechanism and determination of optimal operating conditions.

The conducted theoretical study demonstrates that physical and chemical modification of natural zeolites significantly enhances their adsorption capacity. The integrated use of Langmuir and Freundlich isotherms, as well as kinetic and thermodynamic models, provides a comprehensive explanation of the adsorption mechanism of benzo(a)pyrene and creates a scientific basis for future industrial-scale applications.

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