CHEMICAL TECHNOLOGIES, MATERIALS SCIENCES, METALLURGY
ХИМИЧЕСКИЕ ТЕХНОЛОГИИ, НАУКИ О МАТЕРИАЛАХ, МЕТАЛЛУРГИЯ

UDC 004.942; 544.18
https://doi.org/10.23947/2541-9129-2026-10-2-177-186

Original Theoretical Research

Method for Quantum-Chemical Calculations of Active Centers of the “Sorbent — Pollutant” Molecular Complex in the Search for Ballast Water Filter Components

EDN: YESHPO

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Abstract

Introduction. Pollution of aquatic ecosystems by petroleum products, including the transboundary transport of pollutants from ships' ballast water, requires improvement of cleaning methods. Existing shipboard ballast water management systems are not sufficiently effective in removing dissolved and emulsified hydrocarbons. A promising solution is the use of sorption materials. However, choosing the optimal sorbent for specific pollutants is a challenging task that requires scientific research. In this study, we aimed to demonstrate a quantum chemical modeling technique to predict the effectiveness of the “sorbent — pollutant” interaction using cellulose and typical oil components as examples.

Materials and Methods. A fragment of cellulose (cellobiose) and contaminant molecules: benzene, phenol, and naphthalene were used as a model system. These substances were chosen due to their chemical structure and ability to simulate real environmental pollution. Preliminary optimization of the geometry and calculation of energy parameters were performed using the semi-empirical PM3 method in the GAMESS program. To verify the results, the density functional theory with the B3LYP functional and the 6-31G(d) basis was used. The adsorption energy was calculated as the difference between the total energies of the complex and the isolated components. The active interaction centers were identified based on the analysis of geometric parameters, boundary molecular orbitals (HOMO/LUMO), and charge transfer.

Results. The key electronic characteristics of pollutants were calculated, showing that naphthalene had the highest polarizability (HOMO-LUMO gap 8.43 eV), and phenol had a significant dipole moment (1.14 D). Geometrically and energetically optimal configurations were determined for the cellobiose-benzene complex. It was established that sorption was provided by the formation of weak hydrogen bonds (O...H-C) with distances of 1.85-1.91 Å. The adsorption energy for the most stable configuration was 21.27 kJ/mol, which corresponded to a stable non-covalent interaction. Criteria for the stability of adsorption complexes (energy, structural, electronic) were formulated for the development of preliminary heuristic rules in the decision support system for the selection of sorbents.

Discussion. The developed quantum chemical modeling technique made it possible to quantify the energy and mechanisms of intermolecular interaction in the "sorbent — pollutant" system. It was shown that native cellulose was able to effectively retain nonpolar aromatic hydrocarbons due to dispersion forces and weak hydrogen bonds. The calculated parameters can serve as the basis for a scientifically sound selection of components for ballast water filters and other purification systems, taking into account the type of pollutant, as well as for integration into information and analytical decision support systems.

Conclusion. The results of the work can be integrated into information and analytical decision support systems for the selection of sorbents for ballast water treatment, as well as serve as a basis for further research of modified forms of cellulose.

Keywords: ballast water, oil pollutants, sorption, cellulose, quantum chemical calculations, PM3 method, adsorption energy, molecular modeling

Acknowledgements. The author would like to thank the Head of the scientific project, L.I. Golovatskaya, Cand. Sci. (Eng.), Associate Professor, and A.E. Plastinin, Dr. Sci. (Eng.), Associate Professor, Leading Researcher at the Department of Scientific Research and Digitalization, who conducted an expert assessment of the results of the research together with the author.

For Citation. Tsyguta AN. Method for Quantum-Chemical Calculations of Active Centers of the “Sorbent — Pollutant” Molecular Complex in the Search for Ballast Water Filter Components. *Safety of Technogenic and Natural Systems*. 2026;10(2):177–186. https://doi.org/10.23947/2541-9129-2026-10-2-177-186

Оригинальное теоретическое исследование

Методика проведения квантово-химических расчетов активных центров молекулярного комплекса «сорбент — загрязнитель» при поиске компонентов фильтров балластных вод

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Аннотация

Введение. Загрязнение водных экосистем нефтепродуктами, в том числе трансграничный перенос таких загрязнителей с балластными водами судов, требует доработки имеющихся методов очистки. Существующие судовые системы управления балластными водами недостаточно эффективны для удаления растворенных и эмульгированных углеводородов. Перспективным решением может быть использование сорбционных материалов, однако весьма сложно научно обосновать выбор оптимального сорбента для конкретных типов загрязнителей. В связи с этим целью данной работы является представление методики квантово-химического моделирования для прогнозирования эффективности взаимодействия компонентов в системе «сорбент — загрязнитель» на примере целлюлозы и типичных компонентов нефти.

Материалы и методы. В качестве модельной системы использован фрагмент целлюлозы (целлобиоза) и молекулы-загрязнители (бензол, фенол и нафталин). Эти вещества были выбраны из-за своей химической структуры и способности имитировать реальные загрязнения окружающей среды. Предварительная оптимизация геометрии и расчет энергетических параметров проводились полуэмпирическим методом PM3 в программе GAMESS. Для верификации результатов использовалась теория функционала плотности с функционалом B3LYP и базисом 6-31G(d). Энергия адсорбции рассчитывалась как разность полных энергий комплекса и изолированных компонентов. Активные центры взаимодействия идентифицировались на основе анализа геометрических параметров, граничных молекулярных орбиталей (HOMO/LUMO) и переноса заряда.

Результаты исследования. Рассчитаны ключевые электронные характеристики загрязнителей, показывающие, что нафталин обладает наибольшей поляризуемостью (зазор HOMO-LUMO 8,43 эВ), а фенол — значительным дипольным моментом (1,14 D). Для комплекса «целлобиоза — бензол» определены геометрически и энергетически оптимальные конфигурации. Установлено, что сорбция обеспечивается образованием слабых водородных связей (O…H-C) с расстояниями 1,85–1,91 Å. Энергия адсорбции для наиболее стабильной конфигурации составила 21,27 кДж/моль, что соответствует устойчивому нековалентному взаимодействию. Сформулированы критерии стабильности адсорбционных комплексов (энергетический, структурный, электронный) для разработки предварительных эвристических правил в системе поддержки принятия решений при выборе сорбентов.

Обсуждение. Разработанная методика квантово-химического моделирования позволяет количественно оценивать энергию и механизмы межмолекулярного взаимодействия в системе «сорбент — загрязнитель». Показано, что нативная целлюлоза способна эффективно удерживать неполярные ароматические углеводороды за счет дисперсионных сил и слабых водородных связей. Полученные расчетные параметры могут служить основой для научно обоснованного подбора компонентов фильтров балластных вод и других систем очистки с учетом типа загрязнителя, а также для интеграции в информационно-аналитические системы поддержки принятия решений.

Заключение. Результаты работы могут быть интегрированы в информационно-аналитические системы поддержки принятия решений при выборе сорбентов для очистки балластных вод, а также служить основой для дальнейших исследований модифицированных форм целлюлозы.

Ключевые слова: балластные воды, нефтяные загрязнители, сорбция, целлюлоза, квантово-химические расчеты, метод PM3, энергия адсорбции, молекулярное моделирование

Благодарности. Автор благодарит руководителя научного проекта, кандидата технических наук, доцента Л.И. Головацкую и доктора технических наук, доцента, ведущего научного сотрудника отдела научных исследований и цифровизации А.Е. Пластинина, проводивших экспертную оценку результатов исследования совместно с автором статьи.

Для цитирования. Цыгута А.Н. Методика проведения квантово-химических расчетов активных центров молекулярного комплекса «сорбент — загрязнитель» при поиске компонентов фильтров балластных вод. *Безопасность техногенных и природных систем*. 2026;10(2):177–186. https://doi.org/10.23947/2541-9129-2026-10-2-177-186

Introduction. Pollution of aquatic ecosystems by oil and petroleum products is one of the global environmental issues. Intensive extraction, processing and transportation of hydrocarbons inevitably lead to their entry into surface water and wastewater [1]. This pollution has catastrophic consequences, such as oil films disrupting gas exchange and reducing the concentration of dissolved oxygen, causing hypoxia in aquatic organisms. Water-soluble fractions also have a direct toxic effect, and polycyclic aromatic hydrocarbons are especially dangerous, acting as cellular poisons that can cause acute and chronic poisoning in living organisms [2].

The toxicological effects of petroleum products are complex and multilevel [3]. An analysis of the literature has shown that even sublethal concentrations can cause disorders of physiological functions in aquatic organisms, from cardiac activity and cholesterol metabolism to behavioral reactions such as orientation and avoiding danger [4]. The most vulnerable stages of development are early stages, such as eggs, larvae and juveniles, which are more susceptible to exposure to pollutants, leading to morphological changes, reduced survival, and a decrease in species numbers [2, 4]. In higher animals, including mammals it can cause immunosuppression, reproductive problems, and pathologies of internal organs [4].

It should also be noted that the toxic effect of pollutants varies significantly depending on their chemical composition (fraction). Thus, experimental data show that heavy oil fractions and oil-containing wastes are more toxic to aquatic organisms (for example, to Daphnia magna crustaceans, as shown in [5]) at concentrations one to two orders of magnitude lower than light gasoline fractions. Therefore, risk assessment and development of purification methods need to take into account not only the total amount of petroleum products, but also their molecular composition.

Taking into account the above, a theoretical data collection on the quality of surface water[1] in the Volga River basin has been conducted. As a result, the data have been obtained on several cases of exceeding fisheries standards in recent years [6]. Consequently, when a vessel takes ballast water, it inadvertently carries oil pollutants into the ballast. Afterwards, when the water is discharged in another area, these pollutants are transferred to a new location, creating an additional burden on local ecosystems and increasing the toxic effect on aquatic organisms and disrupting natural biogeochemical processes. In conditions of intense shipping, this poses an environmental risk comparable to that of biological invasions. In addition, there is a risk in areas where oil spills occur, as pollutants, including dissolved and emulsified fractions, can remain in the water for a long time. When these pollutants are removed, they can enter ballast tanks during the cleanup process. This means that ballast water can act as a carrier for existing pollution and transport it across borders.

The International Maritime Organization (IMO) has established discharge standards[2] under the Ballast Water Management Convention with the main goal of controlling the transfer of invasive species. These regulations also indirectly regulate the presence of chemical pollutants, including petroleum hydrocarbons, in ballast water. The IMO-approved ballast water treatment systems primarily aim to disinfect water and destroy biological organisms such as zooplankton, phytoplankton, and bacteria. However, their effectiveness in removing dissolved and emulsified chemical pollutants, particularly petroleum products, is often insufficient [7]. Therefore, it is suggested that modifications or additions to existing ballast water treatment systems that specifically target the removal of chemical pollutants are necessary. Sorption techniques can be used as a solution to the challenge of filling the process module with purification components, which would allow the extraction of a wide variety of petroleum hydrocarbons from water-based environments [7].

[1] State report “On the state and protection of the environment of the Russian Federation”. (In Russ.) URL: https://www.mnr.gov.ru/docs/gosudarstvennye_doklady/o_sostoyanii_i_ob_okhrane_okruzhayushchey_sredy_rossiyskoy_federatsii/ (accessed: 27.01.2026)

[2] International Convention on the Control and Management of Marine Ballast Water and Sediments, 2004 (as amended on November 20, 2020). (In Russ.) URL: https://docs.cntd.ru/document/902152089 (accessed: 03.05.2025).

However, the variety of available sorbents (from natural to synthetic) requires the use of a scientifically based algorithm to determine the choice of a cleansing component. This choice should not only take into account the absorption capacity of the sorbent and its stability under salinity and oscillatory motion, but also economic factors and the selectivity of the material towards specific classes of hydrocarbons.

In this paper, cellulose is considered as a model object for demonstrating the principles of a systematic approach. This renewable biopolymer has the potential for targeted chemical modification and improved hydrophobic properties.

The aim of this research is to demonstrate, using the example of cellulose and typical components of petroleum products, a technique for conducting quantum chemical calculations in order to search for active centers in a purifier and contaminant based on computer modeling of intermolecular interactions and calculation of the sorbent efficiency criterion. The calculated parameters obtained can be used as a quantitative basis for the formation of rules for fuzzy logical inference, which will allow for a scientifically sound selection of materials for specific conditions of ballast water pollution [8].

To achieve this goal, the work is supposed to solve the following tasks:

– to form a set of model molecular systems, including fragments of purifiers (for example, cellulose), as well as representatives of key classes of oil pollutants (for example, benzene, naphthalene, phenol);

– to describe the functional dependencies for calculating the energy parameters of molecular complexes (systems) to confirm the formation of a stable hydrogen bond between molecules, which will determine active centers of the molecules;

– to model molecular complexes and perform a series of quantum chemical calculations to determine the energy and geometric parameters of the formation of molecular complexes as a result of formation of hydrogen bonds;

– based on the performed quantum chemical calculations (task 3), to calculate the energy parameters of molecular complexes to confirm the formation of stable hydrogen bond between the molecules and determine active centers of the molecules;

– to describe functional dependencies for determining the sorption efficiency coefficients for each "sorbent — pollutant" pair.

Materials and Methods. The "cellulose — representative of an oil pollutant" pair was chosen as a model system for the research. Due to the significant size of the cellulose polymer chain, its minimal repeating fragment, cellobiose ($C_{12}H_{22}O_{11}$), was used for quantum chemical modeling. This fragment retained the key functional groups and conformational features of the polymer chain, which made it a representative model that adequately reflected sorption properties of native cellulose [9]. Representatives of the main classes of hydrocarbons were selected as model pollutants: benzene (C_6H_6), phenol (C_6H_6O) and naphthalene ($C_{10}H_8$).

A hierarchy of approximate methods based on the stationary Schrodinger equation for a many-electron system was used to model molecular systems and determine their energy and geometric parameters:

$$\hat{H}\psi = E\psi, \tag{1}$$

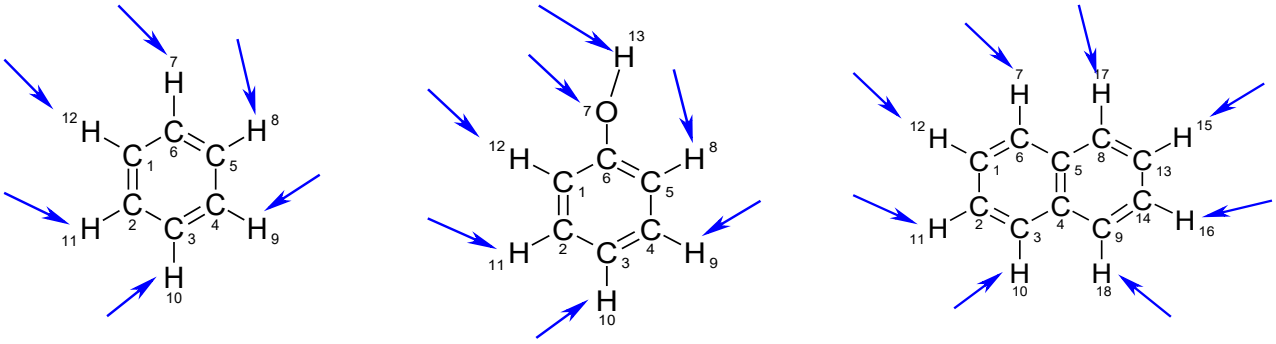
where $\hat{H}$ — Hamiltonian of the system; ψ — wave function; E — stationary state energy [10].

An exact solution to this equation was impossible for systems containing more than two electrons, which required the use of approximate methods, among which methods based on the theory of self-consistent field (SCF) were most widely used. The semi-empirical PM3 method (Parametric Method 3) was used to pre-optimize the geometry of isolated molecules and sort through various spatial orientations of molecules [11]. It was based on the solution of the Roothaan-Hall matrix equation:

$$FC = SC\varepsilon, \tag{2}$$

where F — Fock matrix; C — matrix of coefficients of molecular orbitals; S — overlap matrix; ε — diagonal matrix of orbital energies.

The integrals in F matrix were parameterized based on experimental data, allowing for acceptable accuracy with significantly lower computational costs compared to ab initio methods. Geometry optimization was performed using the eigenvector following (EF) algorithm in the GAMESS program until the gradient norm reached less than 0.001 kcal/(mol Å). Figure 1 shows the result of modeling the molecular interaction of petroleum product components with cellobiose. Arrows indicate the atoms capable of forming bonds.



a) *b)* *c)*

Fig. 1. Interaction pattern of petroleum products components with cellobiose:
a — benzene, *b* — phenol, *c* — naphthalene

The Density Functional Theory (DFT) was used to obtain more accurate energy parameters and analyze the electronic structure [12]. In the Kohn-Sham approach, the problem was reduced to solving a system of one-electron equations:

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\phi_i(r) = \varepsilon_i\phi_i(r), \tag{3}$$

where effective potential $V_{eff}(r) = V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + V_{XC}[\rho(r)]$ included V_{XC} exchange-correlation functional.

In this work, B3LYP [13] hybrid functional with 6-31G(d) basic set was used, which provided a good ratio of accuracy and computational efficiency for organic systems with non-covalent interactions.

Adsorption (bonding) energy ΔE_{ads} for "sorbent (A) — pollutant (B)" molecular complex was the difference between the total energy of optimized complex (AB) and the sum of the energies of its isolated, also optimized components:

$$\Delta E_{ads} = E(AB) - \left[E(A) + E(B)\right]. \tag{4}$$

Negative value of ΔE_{ads} indicated the energy benefits of the complex formation process.

In PM3 method, the total energy of (E_{PM3}) system was formally represented as the sum of two major components: potential energy of electrons (E_{el}) and energy of repulsion of atomic cores (E_{rep}) that were output by the program separately. Therefore, for a strict calculation of ΔE_{ads} within PM3, it was necessary to use the difference form:

$$\Delta E_{ads} = \left[E_{el}(AB) - E_{el}(A) - E_{el}(B)\right] + \left[E_{rep}(AB) - E_{rep}(A) - E_{rep}(B)\right]. \tag{5}$$

To convert the result from electron volts (eV) to kilojoules per mole, a coefficient of $96.485\ kJ\ mol^{-1}$. was used. Thus, the final working formula took the form:

$$\Delta E_{ads}\left(\frac{\text{kJ}}{\text{mol}}\right) = 96.485 \times \left(\left[E_{el}(AB) - E_{el}(A) - E_{el}(B)\right] + \left[E_{rep}(AB) - E_{rep}(A) - E_{rep}(B)\right]\right). \tag{6}$$

Let us consider the calculation of ΔE_{ads} for the most stable configuration of cellobiose complex (Ц) with benzene (Б). After calculating the configuration of the complexes in GAMESS, the following energy values were obtained:

$$E_{el}(\text{Ц}) = -291467.1394\ \text{eV}, \qquad E_{rep}(\text{Ц}) = 218000.000\ \text{eV},$$
$$E_{el}(\text{Б}) = -3162.4272\ \text{eV}, \qquad E_{rep}(\text{Б}) = 2359.6231\ \text{eV},$$
$$E_{el}(\text{ЦБ}) = -294632.5666\ \text{eV}, \qquad E_{rep}(\text{ЦБ}) = 220362.4026\ \text{eV}.$$

Substituting the values in formula (6), we get:

$$\Delta E_{el} = (-294632.5666) - (-291467.1394) - (-3162.4272) = -3{,}0000\ \text{eV},$$

$$\Delta E_{rep} = 220362.4026 - 218000.0000 - 2359.6231 = 2.7795\ \text{eV},$$

$$\Delta E_{ads}(\text{eV}) = -3.0000 + 2.7795 = -0{,}2205\ \text{eV},$$

$$\Delta E_{adc}(\text{kJ/mol}) = 96.485 \times (-0.2205) \approx -21.27\ \text{kJ/mol}.$$

The resulting value of ΔE_{ads} corresponded to the energy of the average hydrogen bond. The active centers of interaction were identified based on the analysis of three aspects:

– finding non-covalent interactions with interatomic distances less than the sum of Van der Waals radii and angles characteristic of hydrogen bonds (O-H…O);

– analysis of boundary molecular orbitals (HOMO/LUMO), band gap (ΔE) and dipole moment (μ) of isolated contaminant molecules to evaluate their polarizability, electron-donating and electron-accepting properties

– calculation of the magnitude and direction of charge transfer (Δq) between fragments using the Mulliken method as an indicator of donor-acceptor interaction.

Results. In order to correctly interpret the sorption mechanisms, we first needed to characterize the key parameters of the isolated contaminant molecules using the PM3 method (Table 1). The values of heat of formation ΔHf reflected different thermodynamic stabilities: phenol was the most stable compound ΔHf = –91.00 kJ/mol, whereas benzene and naphthalene had positive heats of formation.

Electronic parameters were of key importance in predicting reactivity. The energy of the highest occupied molecular orbital (HOMO) characterized the electron-donating ability. The lowest HOMO value in benzene (–9.7 eV) indicated its increased tendency to participate in donor-acceptor interactions as an electron donor. It is important to note that the lowest unoccupied molecular orbital (LUMO) of naphthalene also had a negative energy (–0.41 eV), indicating its ability not only to donate electrons, but also to accept them during the formation of intermolecular complex.

The energy difference between HOMO and LUMO (ΔE), which was a measure of chemical stability and polarizability, was minimal for naphthalene 8.43 eV. Phenol, which had a significant dipole moment (1.14 D) and an average HOMO energy (–9.19 eV), exhibited properties typical of molecules capable of forming directed hydrogen bonds.

Table 1

Quantum chemical characteristics of model pollutants (PM3 method)

Parameters	Benzene (C_6H_6)	Phenol (C_6H_6O)	Naphthalene ($C_{10}H_8$)
Heat of formation, ΔHf (kJ/mol)	99.81	– 91.00	167.70
HOMO energy, E (eV)	– 9.7	– 9.18	– 8.84
LUMO energy, E (eV)	0.37	0.29	– 0.41
HOMO-LUMO gap, ΔE (eV)	10.08	9.47	8.43
Dipole moment, μ (D)	~ 0.01	1.14	~ 0.001

Note: the values were calculated based on the output of the GAMESS program

According to Table 1, the parameters of model pollutants calculated by the PM3 method made it possible to predict their sorption behavior. Naphthalene, which had the highest HOMO energy (– 8.84 eV) and the minimum HOMO-LUMO gap (8.43 eV), demonstrated the greatest polarizability and a tendency to non-covalent interactions. This was due to the presence of two condensed aromatic rings, which created a large intermolecular contact area, and its electrons were distributed throughout the structure, which enhanced dispersion interactions (London forces). Benzene, being a simpler aromatic system, had a lower HOMO value (– 9.70 eV) and a wider HOMO–LUMO gap (10.08 eV), which indicated its lower polarizability and reactivity compared to naphthalene. Of particular interest was phenol, its negative heat of formation (– 91.00 kJ/mol) indicated its thermodynamic stability, while the presence of a hydroxyl group gave the molecule a significant dipole moment (1.14 D) and shifted the interaction mechanism from non-specific dispersion forces to directed hydrogen bonds. The obtained range of values ΔE, naphthalene (8.43 eV) < phenol (9.47 eV) < benzene (10.08 eV), correlated with the expected selectivity of sorption on polar and nonpolar surfaces.

Benzene was chosen as a model pollutant for detailed quantum chemical modeling. This choice was due to the fact that among the aromatic compounds under consideration, benzene was characterized by the maximum band gap (ΔE = 10.08 eV) and, consequently, the lowest polarizability and the minimum tendency to intermolecular interactions (Table 1). Thus, benzene was a more complex object for sorption. The demonstration of sorption efficiency with respect to benzene was a conservative estimate: if a cellulose-based sorbent formed stable complexes with benzene, then obviously more polarizable compounds (naphthalene, its derivatives) and compounds capable of specific interactions (phenol) would be sorbed no worse, and with high probability they would be sorbed better.

Several intermolecular interactions (II) were modeled and optimized for the “cellobiose with benzene” complex (Fig. 2). The analysis of geometric parameters of the optimized structures (Table 2) showed that the stabilization of the complexes in all cases was ensured by the formation of directed hydrogen bonds between the hydrogen atoms of the aromatic ring of benzene and the oxygen atoms of the hydroxyl groups of cellobiose (O...H–C). The distances O...H (1.85–1.91 Å) were in the range typical for weak hydrogen bonds, which confirmed this type of II as the main sorption mechanism. Table 2 shows the relative energies of the system and the magnitude of charge transfer (Δq) for the most stable interactions of the cellobiose-benzene complex.

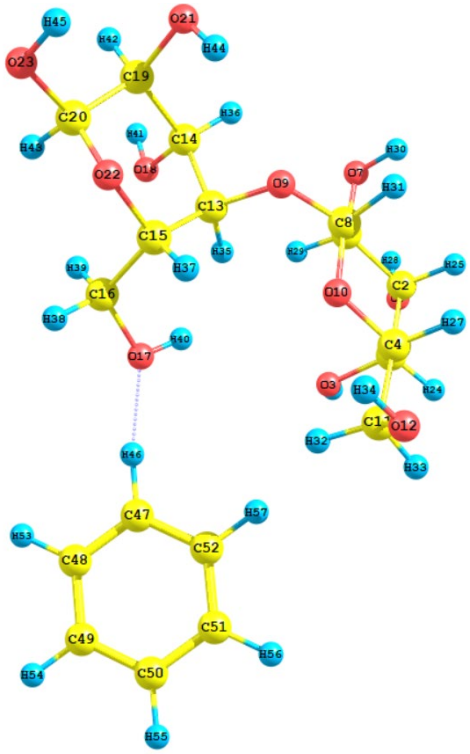


Fig. 2. Molecular interaction of benzene with cellobiose during the formation of O17...H46 hydrogen bond

Table 2

Energy parameters of interaction of the “cellobiose with benzene” complex

II	Type of interaction	ΔE_{ads}, kJ/mol	R, Å	Δq, ē
1	O17…H46	– 21.27	1.85	– 0.155
2	O18…H46	– 16.40	1.91	– 0.143
3	O12…H46	– 13.50	1.85	– 0.157
4	O3…H46	– 13.09	1.86	– 0.138
5	O22…H46	– 12.48	1.87	– 0.154
6	O23…H46	– 9.78	1.88	– 0.132
7	O7…H46	– 9.27	1.88	– 0.122
8	O21…H46	– 9.01	1.88	– 0.129
9	O5…H46	– 8.92	1.90	– 0.121

Note: The symbols used in the description of structures (II) are: R, Å — distance between atoms; ΔE_{ads}, kJ/mol — energy of adsorption; Δq, ē — charge difference of atoms.

The data presented in Table 2 indicated the presence of several local minima on the potential energy surface of the “cellobiose with benzene” complex. The most stable configuration was II1 ΔE_{ads} = –21.27 kJ/mol, which was implemented by A17...H46 hydrogen bond. Configuration II2 E_{ads} = –16.40 kJ/molwith O18...H46 interaction had lower energy benefits, but was also a sustainable sorption complex.

Negative values of charge transfer Δq (from – 0.157 to – 0.121 ē) in all studied IIs indicated a directed electron density flow from the benzene molecule to cellobiose, which was typical for interactions in which oxygen-containing cellulose groups acted as weak electron acceptors. II3 configuration, despite the largest amount of charge transfer (Δq = – 0.157 ē), was characterized by less favorable adsorption energy (ΔE_{ads} = –13.50), which might be due to a violation of optimal geometry due to steric difficulties or suboptimal orientation of the molecule.

The calculation of the absolute adsorption energy carried out according to formula (6) for the most stable configuration II1 gave the value E_{ads} = –21.27 kJ/mol. This value corresponded to the energy of the average hydrogen bond and confirmed thermodynamic benefits of complex formation. The obtained value was in the range typical for stable non-covalent interactions of organic molecules, and was consistent with the literature data for similar systems [14].

The application of the proposed stability criteria to the obtained results showed the following:

1. Energy criterion $\Delta E_{\text{адс}} < -8$ kJ/mol was fulfilled for all the considered complexes of cellobiose with benzene, which indicated sufficient strength of the resulting molecular interaction for practical use in sorption processes.

2. Structural criterion ($R < 2.2$ Å for hydrogen bonds) indicated interactions typical for the formation of hydrogen bonds, which corresponded to the formation of molecular complexes.

3. Electronic criterion $\Delta q \neq 0$ ē was fulfilled for all the configurations studied, confirming the significant contribution of electrostatic interactions to the total adsorption energy.

In the research, a quantum chemical modeling technique was developed and tested to predict [15] the effectiveness of sorbents in ballast water treatment systems. Using the example of the model system “cellobiose (cellulose fragment) — typical oil pollutants (benzene, phenol, naphthalene)”, the tasks set by the authors were solved.

Discussion. The results are of great importance for the development of an algorithm for selecting components for ballast water filters. The revealed relationship between the electronic characteristics of the pollutant (HOMO, ΔE, μ) and the adsorption energy makes it possible to predict the effectiveness of sorbents based on quantum chemical calculations. In particular, for nonpolar aromatic pollutants (benzene, naphthalene), native cellulose demonstrates satisfactory efficiency due to interactions, whereas for polar compounds (phenol), chemical modification of the sorbent may be required to enhance specific interactions. The amount of charge transfer Δq can serve as an additional diagnostic parameter in assessing the sorption mechanism and the selectivity of the material.

A comparison of the results with data from previous studies on molecular complexes [14], where the adsorption energies for systems with hydrogen bonds ranged from – 3.4 to – 20.8 kJ/mol, shows that the interaction of cellobiose with benzene is more energetically advantageous.

In addition to evaluating the effectiveness of sorbents, it is important to consider their cost and safety when making a choice. The cost of the sorbent should be proportionate to its effectiveness and availability. At the same time, we need to analyze not only initial costs but also potential costs for maintenance and disposal. It is crucial that the sorbents we use do not cause negative consequences for the environment both during their use and after their operation. Environmental impact assessments should be an essential part of the process of selecting sorbents. When choosing, we must also consider potential risks to human health associated with certain sorbent use. It is essential to conduct analyses to identify possible releases of harmful substances into the environment. Therefore, the inclusion of these factors in the selection process will not only ensure high purification efficiency, but also promote the sustainable use of sorbents, which aligns with the principles of sustainable development.

Based on the revealed patterns, we can formulate preliminary heuristic rules for the fuzzy inference module.

Conclusion. The conducted research allowed us to draw the following conclusions:

1. A set of representative model systems has been formed.

2. A rigorous methodology for calculating the adsorption energy (ads) was developed and verified based on data from semi-empirical PM3 method (formulas 4–6), which allowed us to obtain a value of 21.27 kJ/mol for the most stable “cellobiose with benzene” II.

3. Key energy and electronic characteristics of pollutants were determined (Table 1), which showed that naphthalene had the greatest tendency to non-covalent interactions (HOMO = – 8.84 eV, ΔE = 8.43 eV).

4. There were three criteria of stability of adsorption complexes: energy $\Delta E_{\text{адс}} < -8$ kJ/mol, structural ($R < 2.2$ Å) and electronic ($\Delta q \neq 0$ ē).

It has been demonstrated that native cellulose is capable of effectively retaining nonpolar aromatic hydrocarbons due to dispersion forces and weak hydrogen bonds, which confirms the potential for its use in ballast water sorption filters. The calculated parameters obtained can serve as a basis for a scientifically sound selection of filter components and their integration into information and analytical decision support systems.

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Conflict of Interest Statement: **the author declares no conflict of interest.**

The author has read and approved the final version of manuscript.

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Конфликт интересов: **автор заявляет об отсутствии конфликта интересов.**

Автор прочитал и одобрил окончательный вариант рукописи.

Received / Поступила в редакцию 13.01.2026
Reviewed / Поступила после рецензирования 09.03.2026
Accepted / Принята к публикации 19.03.2026