Comparison of traditional and fullerene-based adsorbents for extraction of 1,4-dioxane and 2-methyl-1,3-dioxolane from milk

A. I. Kochaev[1,3], R. Razavi[2], S. Kaya[4], M. R. A. Mogaddam[5,6], N. Altunay[4], M. Nemati[5],

K. P. Katin[1,7], K. S. Grishakov[1,7], A. I. Podlivaev[1,7], M. M. Maslov[†,1,7]

†Mike.Maslov@gmail.com

[1]Research Institute for the Development of Scientific and Educational Potential of Youth, Moscow, 119620, Russia
[2]Department of Physical Chemistry, Faculty of Science, University of Jiroft, Jiroft, 7867161167, Iran
[3]Ulyanovsk State University, Ulyanovsk, 432017, Russia
[4]Sivas Cumhuriyet University, Department of Biochemistry, Sivas, 58140, Turkey
[5]Food and Drug Safety Research Center, Tabriz University of Medical Science, Tabriz, 5165665931, Iran
[6]Pharmaceutical Analysis Research Center, Tabriz University of Medical Science, Tabriz, 5165665931, Iran
[7]National Research Nuclear University MEPhI, Moscow, 115409, Russia

Using density functional methods, the results of the analysis of traditional adsorbents and adsorbents based on nanosized particles capable of trapping 1,4-dioxane and 2-methyl-1,3-dioxolane molecules in milk are presented. We considered the following interacting compounds: 1,4-dioxane — primary amine, 1,4-dioxane — secondary amine, 1,4-dioxane — fullerene C_{20}, 1,4-dioxane — a fragment of the structure of activated carbon, 2-methyl-1,3-dioxolane — primary amine, 2-methyl-1,3-dioxolane — secondary amine, 2-methyl-1,3-dioxolane — fullerene C_{20}, 2-methyl-1,3-dioxolane — a fragment of the structure of activated carbon. We determined the optimal configurations of the corresponding interacting structures, estimated their binding energies and chemical potentials. The highest binding energy was obtained for 1,4-dioxane adsorbed on C_{20} fullerene. At the same time, the energy gaps between the occupied HOMO and unoccupied LUMO molecular states were calculated, which makes it possible to characterize the reactivity and stability of molecules. Compounds of 1,4-dioxane and 2-methyl-1,3-dioxolane with amines have rather large gaps HOMO-LUMO. Using the concept of the electronic localization function, we found that a covalent bond is formed between 1,4-dioxane and C_{20} fullerene with a sufficiently high degree of electron localization in the bond region. In other cases, the value of the localization function indicates the absence of a chemical bond between the compounds. The proposed study gives recommendations on the adsorption of 1,4-dioxane and 2-methyl-1,3-dioxolane for further solid-phase microextraction, which will allow them to be found in milk by gas chromatography using a flame ionization detector.

Keywords: adsorption, dioxane, density functional theory, solid-phase microextraction.

УДК: 544.723

Сравнение традиционных адсорбентов и адсорбентов на основе фуллерена для детектирования 1,4-диоксана и 2-метил-1,3-диоксолана в молоке

Кочаев А. И.[1,3], Разави Р.[2], Кайя С.[4], Могаддам М. Р. А.[5,6], Алтунай Н.[4], Немати М.[5],

Катин К. П.[1,7], Гришаков К. С.[1,7], Подливаев А. И.[1,7], Маслов М. М.[†,1,7]

[1]Научно-исследовательский институт Проблем развития научно-образовательного потенциала молодежи, Москва, 119620, Россия
[2]Кафедра физической химии, Факультет естественных наук, Университет Джирофта, Джирофт, 7867161167, Иран
[3]Ульяновский государственный университет, Ульяновск, 432017, Россия
[4]Сивасский республиканский университет, Факультет биохимии, Сивас, 58140, Турция
[5]Исследовательский центр безопасности пищевых продуктов и лекарств, Тебризский университет медицинских наук, Тебриз, 5165665931, Иран
[6]Исследовательский центр фармацевтического анализа, Тебризский университет медицинских наук, Тебриз, 5165665931, Иран
[7]Национальный исследовательский ядерный университет «МИФИ», Москва, 115409, Россия

В настоящей статье с использованием методов теории функционала плотности представлены результаты анализа традиционных адсорбентов и адсорбентов на основе наноразмерных частиц, способных улавливать молекулы 1,4-диоксана и 2-метил-1,3-диоксолана в молоке. Мы рассмотрели ряд взаимодействующих соединений, в том числе 1,4-диоксан — первичный амин, 1,4-диоксан — вторичный амин, 1,4-диоксан — фуллерен C_{20}, 1,4-диоксан — фрагмент структуры активированного угля, 2-метил-1,3-диоксолан — первичный амин, 2-метил-1,3-диоксолан — вторичный амин, 2-метил-1,3-диоксолан — фуллерен C_{20}, 2-метил-1,3-диоксолан — фрагмент структуры активированного угля. Нами определены оптимальные конфигурации соответствующих взаимодействующих структур, оценены их энергии связи и химические потенциалы. Наибольшее значение энергии связи зафиксировано для 1,4-диоксана, адсорбированного на фуллерене C_{20}. Вместе с тем, рассчитана величина энергетической щели между наивысшими занятыми HOMO и наинизшими свободными LUMO молекулярными состояниями, что позволяет охарактеризовать реакционную способность и стабильность молекул. Соединения 1,4-диоксана и 2-метил-1,3-диоксолана с аминами имеют достаточно большую щель HOMO-LUMO. С использованием представления об электронной функции локализации, мы обнаружили, что между 1,4-диоксаном и фуллереном C_{20} образуется ковалентная связь с достаточно высокой степенью локализации электронов в области связи. В остальных случаях значение функции локализации указывает на отсутствие химической связи между соединениями. Предлагаемое исследование дает рекомендации по адсорбции 1,4-диоксана и 2-метил-1,3-диоксолана в целях дальнейшей твердофазной микроэкстракции, что позволит находить их в молоке методом газовой хроматографии с применением пламенно-ионизационного детектора.

Ключевые слова: адсорбция, диоксан, теория функционала плотности, твердофазная микроэкстракция.

1. Introduction

The planetary deterioration of the ecological situation is inextricably linked with the deterioration of the quality of food, the safety of which is the key to preserving human health. It is especially important to preserve the naturalness and purity of baby food as a guarantee of the preservation and transmission of the "correct" genetic information. One of the environmental pollutants is 1,4-dioxane, the chemical formula of which is $C_4H_8O_2$. It is widely used in industry as a strong solvent in the production of adhesives, textiles, papers, lacquers, pharmaceuticals and other chemicals, but at the same time, it is a toxic substance, a potential carcinogen that can damage the central nervous system, liver, and kidneys [1]. 1,4-dioxane is found in drinking water and the ambient air. In addition, it is known that in the context of preserving children's health, 1,4-dioxane can be transmitted to infants during lactation. According to pharmacokinetic models [2], it was shown that 1,4-dioxane, along with carbon tetrachloride, methylchloroform, perchloroethylene, has the property of easily binds to milk, which is inhaled from the ambient air to nursing mothers. In this regard, the problem of determining foreign chemical inclusions and maintaining the chemical purity of breast milk is relevant and promising. The detection of 1,4-dioxane is an independent task and can be considered in conjunction with the detection of 2-methyl-1,3-dioxolane since the latter is the most frequent derivative of 1,4-dioxane, often obtained as a result of the decomposition of 1,4-dioxane and indicates its presence. Finding two substances at once in breast milk and milk products for children will more accurately characterize its purity. It is important to be able to detect these two substances simultaneously.

Due to the high solubility of 1,4-dioxane in water, its detection seems to be a serious problem [3]. There are various physical and chemical methods of analysis. Standard analytical methods based on closed-loop stripping analysis [4] are not suitable to determine 1,4-dioxane owing to taste and odor are almost absent [3]. The physicochemical method for separating substances, based on the distribution of the components of the analysed mixture between two immiscible phases moving relative to each other (the gas chromatography method), can be very reliable in this case. 1,4-dioxane, which has the properties of volatility and thermal stability, meets the requirements of this method. The following detectors can be used to continuously measure the concentration of substances at the outlet of the chromatographic column: thermal conductivity detector, electron capture detector, mass spectrometry, and others. A detector for the determination of 1,4-dioxane must simultaneously combine the properties of versatility, non-destructive measurements, and high sensitivity to organic compounds. The Flame ionization detector reacts to all compounds that can be ionized by a flame and are a dedicated organic compound detection tool. To apply this method, a preliminary concentration of dioxane and 2-methyl-1,3-dioxolane is required.

To pre-concentrate the dioxane and dioxolane, one of three methods must be used: liquid-liquid extraction (LLE), purge and trap (PT), and solid-phase extraction [5]. The PT pre-concentration method requires extended purge time or additional heat. The reported limit for the PT method, observed in [3], was 150 ng/L. The detection limit in the LLE method was 200 ng/L [6]. The separation of solid-phase mixtures using solid sorbents in the SPE method allows one to increase the dioxane concentration to 1 μg/L [7–9]. A variation of the SPE method is the solid-phase microextraction (SPME) with involves the use of a fibre coated with an extracting phase. The SPME approach can be effectively used in combination with gas chromatography due to improvement in time-saving, economic factors, and detection limits [10].

The stationary phase in the gas chromatography method is solid particles, namely adsorbents with a high specific surface area (10–1000 m²/g). The search for such adsorbents by the methods of quantum chemistry is the subject of this article, i. e., we hope to obtain a comparative picture of the degree of adsorption of dioxane and methyl-1,3-dioxolane on known

materials and, based on the obtained data, to give appropriate recommendations for the selection of adsorbents based on quantum chemistry. We will take activated carbon, amines, fullerenes, and other carbon nanoparticles as the analysed adsorbents. Activated carbon as a well-known sorbent is used in the field of pharmacology, in the food industry, in the military, in devices for purifying drinking water [11,12], and in many other areas of life. The effectiveness of primary and secondary amines as adsorbents was discussed in [13], where, in particular, it was shown that the processes of adsorption and desorption for the primary, secondary, and tertiary amines proceed in opposite directions. The study of hybrid materials based on mixed amines and oxides for the capture and separation of CO_2 from bio-hydrogen was carried out in [14]. Further, fullerenes are stable, biocompatible, and highly reproducible nanoparticles. It was shown in [15,16] that fullerenes, fullerene-, graphene-like materials [17], due to their large specific surface area, can chemically bind a large number of particles. Although C_{60} and nanotubes are more suitable due to their larger area, we consider C_{20} as the minimum fullerene, it is the most curved and therefore the most active. The efficiency of adsorption using functionalized nanoparticles by different groups is also an interesting subject for research.

2. Computational details

The considered atomic model was driven to energy-optimal configurations using the GAMESS software package [18]. Based on the density functional theory using the set of basis functions B3LYP/6-311G, the diameter of the molecules, their total energies corresponding to a given local energy minimum, and the bond lengths were calculated. All structures are optimized while a Hellman-Feynman force convergence exceeds 10^{-2} eV/Å. Iteration tolerance is 10^{-5}. The dispersion interaction was taken into account by the DFT-D2 method of Grimme [19]. The density function theory method is also used to calculate the HOMO-LUMO sites and Electron Localization Function (ELF). The full visualization process is carried in the ChemCraft package.

3. Models

Fig. 1 shows the models for the considered 1,4-dioxane and 2-methyl-1,3-dioxolane, primary amines, secondary amines, fullerene C_{20}, and activated carbon. All of them considered molecules were optimized as described above. The dark grey balls denote the carbon atoms, the light grey balls denote the hydrogen atoms, the red balls denote the oxygen atoms, and the blue balls denote the nitrogen atoms.

Further, we constructed the atomistic models of interacting structures: 1,4-dioxane — primary amine, 1,4-dioxane — secondary amine, 1,4-dioxane — fullerene C_{20}, 1,4-dioxane — a fragment of the structure of activated carbon, 2-methyl-1,3-dioxolane — primary amine, 2-methyl-1,3-dioxolane — secondary amine, 2-methyl-1,3-dioxolane — fullerene C_{20}, 2-methyl-1,3-dioxolane — a fragment of the structure of activated carbon. We performed the optimization procedure again. The initial configurations of the interacting
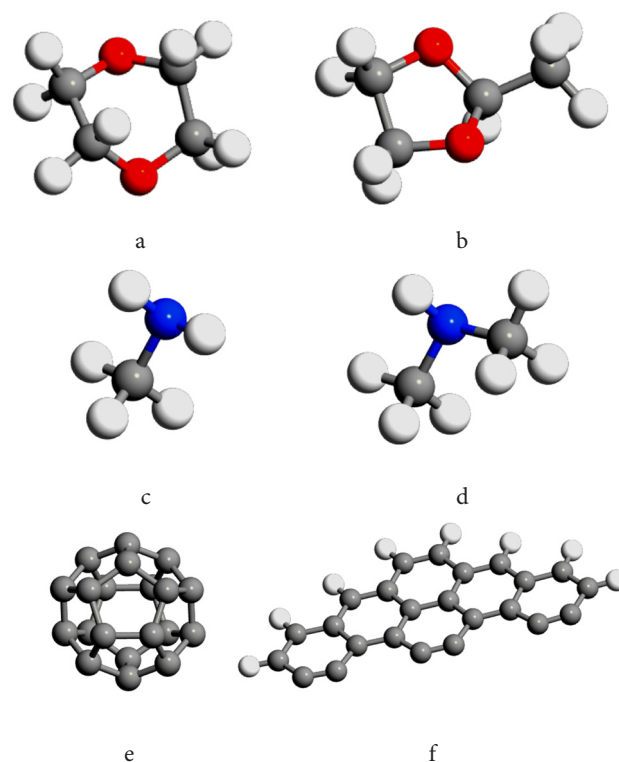

Fig. 1. (Color online) Atomic models of optimized structures: 1,4-dioxane (a), 2-methyl-1,3-dioxolane (b), primary amine (c), secondary amine (d), fullerene C_{20} (e), fragment of the structure of activated carbon (e).

structures were chosen so that the space between them contained as many atoms as possible.

4. Results and Discussions

The binding (adsorption) energy of 1,4-dioxane and 2-methyl-1,3-dioxolane molecules on primary and secondary amines, fullerene C_{20}, and a fragment of the structure of activated carbon was given by [20]

$$E_b = E_{tot} - (E_{mol} + E_{ads}),$$

where E_{tot} is the total optimized energy of the complex interacting structures, E_{mol} is the energy of the free, relaxed 1,4-dioxane molecule (or 2-methyl-1,3-dioxolane molecule), and E_{ads} is the same energy one of four adsorbents.

As shown in [21], the density functional theory allows getting a set of physical quantities. One of them is the HOMO-LUMO gap. It is defined as the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital [21]. So, the optimized parameters for the adsorption of the 1,4-dioxane molecule and 2-methyl-1,3-dioxolane molecule on the four adsorption species were tabulated in Table 1.

As shown in Table 1, the largest bonding was found for 1,4-dioxane — fullerene C_{20} because the $E_b = -0.435$ eV. At the same time, 2-methyl-1,3-dioxolane and secondary amine are weakly bonded. 1,4-dioxane and 2-methyl-1,3-dioxolane have a general tendency when adsorbed on the considered materials, namely, the binding energies of these molecules with "pure" carbon materials (fullerene C_{20} and activated carbon) are higher than with amines. In general, obtained

values are close to the adsorption energy of oxygen molecules physisorbed on two-dimensional tungsten disulfide [22]. As to the HOMO-LUMO gap, the compounds of 1,4-dioxane and 2-methyl-1,3-dioxolane molecules with amines have a large HOMO-LUMO gap. The HOMO-LUMO gap is reduced as one moves to other adsorbents.

To understand the bonding character of the considered interacting structures, we calculated the ELF as [23]

$$ELF = \frac{1}{1+\left(D/D_0\right)^2},$$

where D is the kinetic energy density of the considered system and D_0 is the kinetic energy density of a homogeneous electron gas. If ELF takes values close to 0, then such space regions contain not localized electrons and, conversely, if the value is 1, high localization of electrons can be observed. [23]. Fig. 2 shows the results of isosurfaces of ELF for all interacting structures.

As shown in Fig. 2 c, the high electron localization is reached between 1,4-dioxane and fullerene C_{20}. In remain cases, ELF is in the range from 0.07 to 0.15, indicating the absence of covalent bonding between them. These captures are obtained for the same levels of ELF. On the contrary, Fig. 3 shows the results of maps of ELF for all interacting structures when one sees different values of ELFs. These images are designed to show the shortest distance between two molecules. The figure clearly shows the areas of covalent bonding inside the molecules depicted in red colour. At the same time, intermolecular regions considered structures (except the 1,4-dioxane — fullerene C_{20}) are marked in blue and green.

5. Conclusions

Quantum chemistry is a powerful tool for predicting the properties of new materials and their compounds. But often, the results obtained in the course of quantum chemistry turn out to be divorced from practice. In this study, we have provided an appropriate link, since the obtained results will help to understand which classical or new materials can be used for the effective adsorption of toxic 1,4-dioxane and

Table 1. The optimized parameters for the adsorption of the 1,4-dioxane molecule and 2-methyl-1,3-dioxolane molecule on the four adsorption species: binding energies E_b, shortest distance l_s between the interacting compounds, chemical potentials μ, and HOMO-LUMO gap Δ_{HL}.

| Interacting structures	Shortest distance l_s, Å	Binding energy E_b, eV	Chemical potentials μ, eV	HOMO-LUMO gap Δ_{HL}, eV
1,4-dioxane — primary amine	2.25	−0.291	−2.35	6.20
1,4-dioxane — secondary amine	2.52	−0.247	−2.19	6.44
1,4-dioxane — fullerene C_{20}	1.36	−0.435	−4.42	0.65
1,4-dioxane — activated carbon	2.97	−0.350	−4.68	2.19
2-methyl-1,3-dioxolane — primary amine	2.42	−0.297	−2.28	5.94
2-methyl-1,3-dioxolane — secondary amine	2.09	−0.185	−2.38	6.51
2-methyl-1,3-dioxolane — fullerene C_{20}	2.45	−0.397	−4.66	0.71
2-methyl-1,3-dioxolane — activated carbon	2.83	−0.301	−4.80	1.64
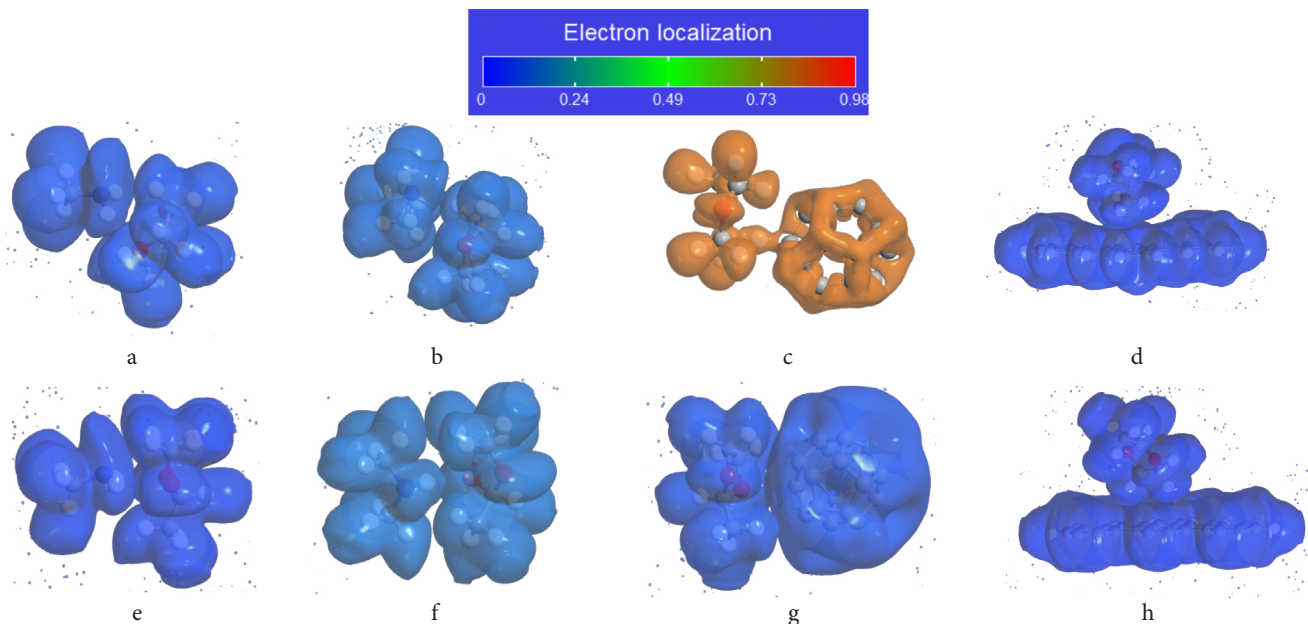
Fig. 2. (Color online) Isosurfaces of ELF: 1,4-dioxane — primary amine (a), 1,4-dioxane — secondary amine (b), 1,4-dioxane — fullerene C_{20} (c), 1,4-dioxane — fragment of the structure of activated carbon (d), 2-methyl-1,3-dioxolane — primary amine (e), 2-methyl-1,3-dioxolane — secondary amine (f), 2-methyl-1,3-dioxolane — fullerene C20 (g), 2-methyl-1,3-dioxolane — fragment of the structure of activated carbon (h).
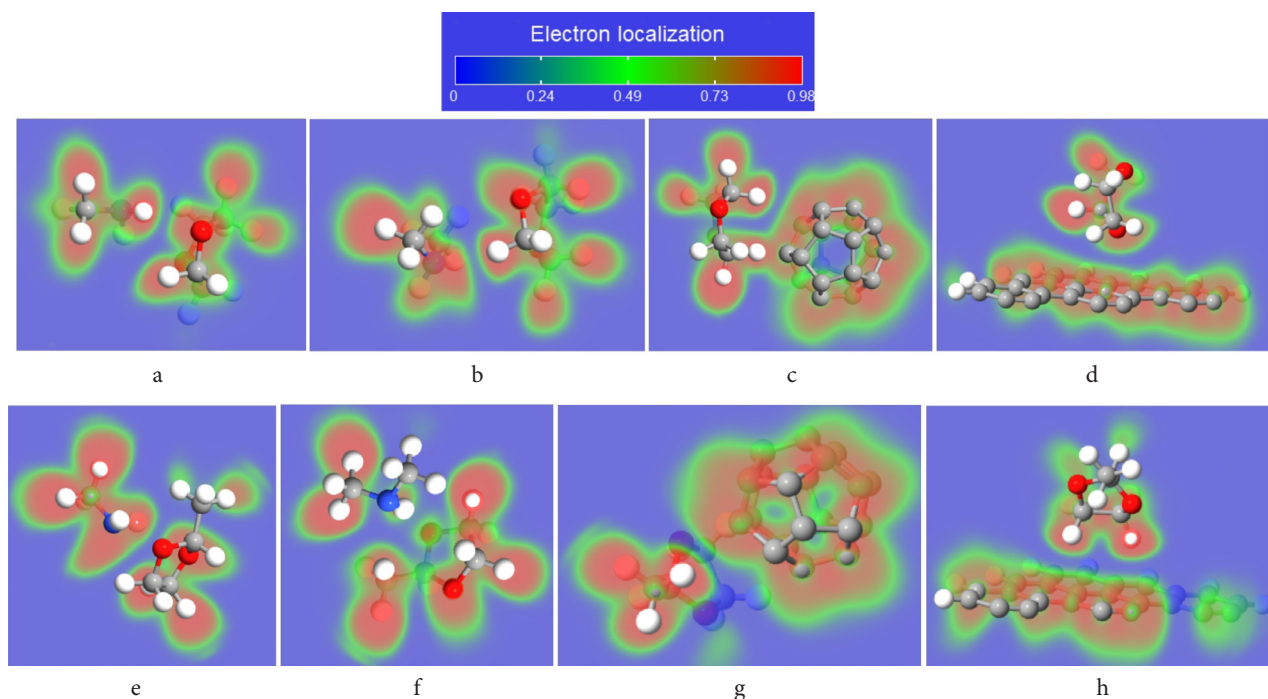
Fig. 3. (Color online) Maps of ELF: 1,4-dioxane — primary amine (a), 1,4-dioxane — secondary amine (b), 1,4-dioxane — fullerene C_{20} (c), 1,4-dioxane — fragment of the structure of activated carbon (d), 2-methyl-1,3-dioxolane — primary amine (e), 2-methyl-1,3-dioxolane — secondary amine (f), 2-methyl-1,3-dioxolane — fullerene C_{20} (g), 2-methyl-1,3-dioxolane — fragment of the structure of activated carbon (h).

2-methyl-1,3-dioxolane. This information will help to carry out solid-phase microextraction and find them in milk using gas chromatography with a flame ionization detector method.

References

1. T. Kasai, H. Kano, Y. Umeda, T. Sasaki, N. Ikawa, T. Nishizawa, K. Nagano, H. Arito, H. Nagashima, S. Fukushima. Inhalation Toxicology. 21, 889 (2009). Crossref
2. J. Fisher, D. Mahle, L. Bankston, R. Greene, J. Gearhart. Am. Ind. Hyg. Assoc. J. 58, 425 (1997). Crossref
3. M. Sun, C. Lopez-Velandia, D. R. U. Knappe. Environmental Science & Technology. 50, 2246 (2016). Crossref
4. L. I. Osemwengie, S. Steinberg. J Chromatogr A. 993, 1 (2003). Crossref
5. G. Carrera, L. Vegué, M. R. Boleda, F. Ventura. J Chromatogr A. 3, 1487 (2017). Crossref
6. Y.-M. Park, H. Pyo, S.-J. Park, S.-K. Park. Analytica Chimica Acta. 548, 109 (2005). Crossref
7. P. E. Grimmett, J. W. Munch. Journal of Chromatographic Science. 47, 31 (2009). Crossref
8. D. K. Stepien, P. Diehl, J. Helm, A. Thoms, W. Püttmann. Water Research. 48, 406 (2014). Crossref
9. S. M. Simonich, P. Sun, K. Casteel, S. Dyer, D. Wernery, K. Garber, G. Carr, T. Federle. Integrated Environmental Assessment and Management. 9, 554 (2013). Crossref
10. G. Vas, K. Vékey. J. Mass Spectrom. 39, 233 (2004). Crossref
11. S. Biniak, G. Szymański, J. Siedlewski, A. Świątkowski. Carbon. 35, 1799 (1997). Crossref
12. J. P. Boudou, M. Chehimi, E. Broniek, T. Siemieniewska, J. Bimer. Carbon. 41, 1999 (2003). Crossref
13. N. Ravi, S. A. Anuar, N. Y. M. Yusuf, W. N. W. R. Isahak, M. S. Masdar. Materials Research Express. 5, 055501 (2018). Crossref
14. Y. G. Ko, S. S. Shin, U. S. Choi. J. Colloid Interface Sci. 361, 594 (2011). Crossref
15. A. V. Eletskii. Physics-Uspekhi. 47, 1119 (2004). Crossref
16. R. A. Brazhe, I. S. Olenin. J. Phys.: Conf. Ser. 345, 012039 (2012). Crossref
17. A. I. Kochaev. AIP Advances. 7, 025202 (2017). Crossref
18. M. W. Schmidt et al. J. Comput. Chem. 14, 1347 (1993). Crossref
19. S. Grimme, J. Antony, S. Ehrlich, H. Krieg. J. Chem. Phys. 132, 154104 (2010). Crossref
20. H. Y. Ammar, E.-S. R. H. El-Gharkawy. European Journal of Scientific Research. 120, 401 (2014).
21. M. A. Gimaldinova, M. M. Maslov, K. P. Katin. CrystEngComm. 20, 4336 (2018). Crossref
22. F. R. Bagsican, A. Winchester, S. Ghosh, X. Zhang, L. Ma, M. Wang, H. Murakami, S. Talapatra, R. Vajtai, P. M. Ajayan, J. Kono, M. Tonouchi, I. Kawayama. Scientific Reports. 7, 1774 (2017). Crossref
23. A. Kochaev, R. Meftakhutdinov, R. Sibatov, K. Katin, M. Maslov, V. Efimov. Appl. Surf. Sc. 562, 150150 (2021). Crossref