Features of the separation of difficultly separable organic compounds by liquid-phase adsorption on HKUST-1-type framework structures

I G Bratchikova, S O Kovtun, E B Markova, N Yu Isaeva, A G Cherednichenko
Peoples’ Friendship University of Russia (RUDN University), 117198, Moscow, Russia

E-mail: bratchikova_ig@pfur.ru, ebmarkova@gmail.com

Abstract. The work is devoted to the study of the adsorption characteristics of MOF based on Cu\(^{2+}\) for the processes of liquid-phase adsorption of aromatic organic compounds. The metal organic framework HKUST-1 based on Cu\(^{2+}\) ions with 1,3,5-benzenethricarboxylic acid as ligands was studied and its adsorption parameters were established, in particular, retention times for various substances from a number of chlorophenols, efficiency and resolution of chromatographic HKUST-1 based columns for selected compounds.

1. Introduction
For the separation of difficult to separate liquid-phase systems, such complex-porous zeolite structure systems as magnesium impregnated NaY zeolites, which can be advantageously used for glucose isomerization to fructose, are widely used today. [1].

Unlike hydrophilic zeolites of the FAU type, their hydrophobic dealuminated analogue used here can separate disaccharides, the delay of which can significantly exceed the monosaccharide content [2].

Aluminum-containing zeolites (ZSM-5-11 and ZSM-5-36) with a negatively charged framework have much higher adsorption abilities than zeolites without aluminum due to the additional electrostatic attractive interaction [3].

Further improvement of the structure for separating difficultly separated mixtures led to the appearance of zeolite imidazolate scaffolds (ZIF) forming the MOF subfamily. In ZIF, metal cations (e.g. Zn\(^{2+}\), Co\(^{2+}\) and Cu\(^{2+}\)) are tetrahedrally coordinated by imidazolate linkers, which often leads to a relative thermally and hydrothermally stable network showing zeolite topologies. A well-known ZIF structure is ZIF-8, in which 2-methylimidazolate anions are bound to Zn\(^{2+}\) cations, which leads to an expansion of the SOD structure. Another known MOF structure is ZIF-7, where Zn\(^{2+}\) ions are bonded to each other by benzimidazolate anions.

Therefore, in a relatively short time, the first MOF membranes with molecular sieve properties were developed.

According to theoretical predictions, zeolite-like organometallic compounds should have greater selectivity with respect to the components in the mixture and not be inferior in sorption performance to zeolite sorbents. Due to the presence of organic and inorganic particles in MOFs, new possibilities arise for the separation of isomers, as well as for increasing the selectivity of reactions.
These crystalline hybrid materials are composed of inorganic subunits (metal clusters, chains or layers) linked by organic polycomplexing fragments (carboxylates, azolates, imidazolates) [4-8]. Their attractiveness lies in an unprecedented huge range of chemical and physical properties that can be investigated, where the vast majority of the elements of the periodic table were used in a particular material.

Therefore, the aim of this work was to study the features of the separation of organic compounds by liquid-phase adsorption on HKUST-1 frame structures.

2. Results and discussion

The analysis was performed using an Agilent 1200 liquid chromatograph with an eluent speed of 0.5 ml/min, wavelength $\lambda = 254$ nm, pressure from 7 to 11 bar. Detection was performed using fluorimetric (FLD) and UV detectors (DAD). As the stationary phase, the sorbent HKUST-1 synthesized in the laboratory of the development and research of polyfunctional catalysts (No. 14) of the INEOS RAS was used. The HKUST-1 obtained by the hydrothermal method has an octahedral shape (Figure 1) and has a rough surface with a particle size of 5 $\mu$m (column 20 × 4 mm). The analysis was carried out in three thermostating modes: 25, 35, and 45 °C. The sample was introduced after preliminary dissolution in acetonitrile. Methanol CH$_3$OH, acetonitrile CH$_3$CN and tetrahydrofuran (THF) (CH$_2$)$_4$O were used as eluents.

Figure 1: Snapshots of FE-SEM MOF HKUST-1

The choice of the best eluent as the mobile phase was carried out by experimental selection of the most different retention times. Such features were taken into account that component A provides mainly the transport function for moving already desorbed substances in the column, component B, on the contrary, being a competitor of the separated substances in sorption processes, can displace them from the sorbent in the eluent volume and, thereby, significantly reduce their retention time. By increasing the proportion of component B in solvent A, it is possible to smoothly change the eluting strength of this mixture and to achieve almost any value in the interval of the eluotropic series from A to B.

For analysis, Sigma-Aldrich solvents for HPLC ≥99.9% were used as the mobile phase in reverse phase liquid chromatography.

The degree of separation of two substances (or resolution) is determined directly from the chromatogram and is calculated as the ratio of the difference in retention times to half the sum of the peak widths at the baseline level:

$$R = 2 \times (t_{R1} - t_{R2}) / (w_1 + w_2).$$

Efficiency was calculated by the peak in the chromatogram:
N = 5,545×(t_R/w½)^2, N = 16×(t_R/w_s)^2, N = 4×(t_R/w_{2\sigma})^2,

gde N – efficiency; w½ – peak width at half height, min; w_s – peak width at the base, min; w_{2\sigma} – peak width at a height of 2\sigma, min; t_R – retention time, min.

When it comes to analytical applications, the column is characterized by efficiency (the number of theoretical plates). In the case of the theory of chromatography, its inverse, which is called height equivalent to theoretical plate, HETP, H:

H = L/N,

where H – HETP, mm; L – column length, mm; N – column efficiency.

As a result of the studies, it was found that when methanol CH₃OH, acetonitrile CH₃CN and tetrahydrofuran (THF) (CH₂)₄O were used as eluents, a clear dependence of the dead retention time on the volatility of the eluent was traced (figure 2), which shifts to the region of small times with increasing temperature column temperature control at 10 °C.

![Figure 2. Temperature dependence of dead time retention of various eluents](image)

It was found that at relatively high eluent flow rates, an increase in temperature to 45 °C leads to a twofold increase in mass transfer efficiency (decrease in HETP) regardless of the volatility of analytes (figure 3). The effect of the influence of longitudinal diffusion on the blurring of zones of shared analytes does not appear at low temperature. As analytes, a difficultly separable mixture of chlorophenol derivatives was used.

However, such a lack of influence of analyte volatility on HETP occurs at sufficiently high concentrations of acetonitrile, which is in good agreement with generally accepted laws.
| №  | Name of substance       |
|----|-------------------------|
| 1  | 2,3-dichlorophenol      |
| 2  | 2,6-dichlorophenol      |
| 3  | 2,5-dichlorophenol      |
| 4  | 2,4-dichlorophenol      |
| 5  | 3,4-dichlorophenol      |
| 6  | 3,5-dichlorophenol      |
| 7  | 2,3,5-trichlorophenol   |
| 8  | 2,3,6-trichlorophenol   |
| 9  | 2,4,5-trichlorophenol   |
| 10 | 2,4,6-trichlorophenol   |
| 11 | 4-chlorophenol          |

**Figure 3**: Temperature dependence of HETP of various analytes with eluents CH$_3$OH (a), CH$_3$CN (b), (CH$_2$)$_4$O (c).

Further research on the effect of temperature on chromatographic characteristics, such as the selectivity coefficient and the degree of separation showed that with increasing temperature the selectivity worsens and does not depend on the use of various solvents as eluent.

An increase in temperature to 45 °C with the use of any eluent led to the fact that the analytes did not separate. A similar effect is observed for the degree of separation, so it was advisable to choose only the most effective temperature for thermostating the column. Guided by the principles of time costs and the degree of separation, a temperature of 35 °C was chosen.

From the graph in figure 4 it is seen that the best separation is observed when using acetonitrile CH$_3$CN as an eluent. The eluting strength of solvents decreases in the series acetonitrile - methanol - THF. When using THF, a seemingly anomalous increase in acid retention is observed in comparison with all other solvents. Perhaps this is due to the high ability of THF molecules to be acceptors in the formation of hydrogen bonds with analytes and with modifier molecules on the surface of the sorbent.

The selectivity of the separation of compounds using methanol as a representative of a biphilic solvent as an eluent is sufficient to be used in the separation of organic mixtures of a phenol-substituted series.
3. Conclusion
The features of the separation of organic compounds by liquid-phase adsorption on HKUST-1 frame structures were studied. When selecting an eluent for chromatographic separation of chlorophenols by HPLC, it was found that, in combination with acetonitrile, the mobile phase in the form of MeCN showed the best separation of the mixture of the following composition: 2,3-dichlorophenol, 2,6-dichlorophenol, 2,5-dichlorophenol, 2,4-dichlorophenol, 3,4-dichlorophenol, 3,5-dichlorophenol, 2,3,5-trichlorophenol, 2,3,6-trichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 4-chlorophenol. It was found that the best ratio of retention times is achieved when MeCN is used as an eluent. The found constants for the separation of substances in the stationary phase of the HKUST-1 type showed the possibility of using this type of sorbent as the stationary phase. The efficiency of the sorbent from HKUST-1 frame structures with respect to a mixture of chlorophenols was sufficient to include this type of sorbent in the list of stationary phases in HPLC.

References
[1] Graça I, Bacariza M C, Fernandes A, Chadwicka D 2018 J. Applied Catalysis B- Environmenta 224 660-670
[2] Wach W, Buttersack C, Buchholz K 2018 Journal of Chromatography A 1576 101-112
[3] Ling Zanga, Xin Weng, Xiaolei Qu, Heyun Fu, Hui Liu, Shourong Zheng, Zhaoyi Xu, Dongqiang Zhu 2019 J. Microporous and Mesoporous Materials 280 315-323
[4] Fe’rey G, 2008 J. Chem. Soc. Rev. 37 191-214
[5] Hoskins B F, Robson R 1989 J. Am. Chem. Soc. 111 5962-5964
[6] Yaghi O.M, Li H 1985 J. Am. Chem. Soc. 117 10401-10402
[7] Kondo M, Yoshitomi T, Seki K, Matsuzaka H, Kitagawa S 1997 J. Angew. Chemie Int. Ed. English 36 1725-1727
[8] Fe’rey G 2001 J. Ecumenism in chemistry, Chem. Mater 13 3084-3098.