Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2022, **32**, 661–663

Mendeleev Communications

Zr^{IV} metal–organic framework based on terephthalic acid and 1,10-phenanthroline as an adsorbent for solid phase extraction of tetracycline antibiotics

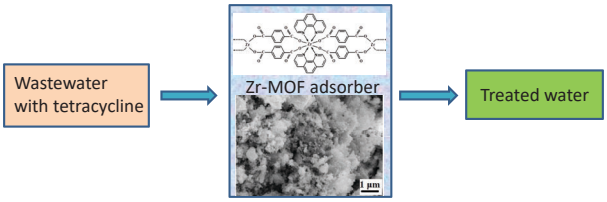
Oxana V. Kharissova,*[a] Vladimir A. Zhinzhilo,[b] Julia D. Bryantseva,[b] Igor E. Uflyand[b] and Boris I. Kharisov[a]

[a] *Universidad Autónoma de Nuevo León, 66455 San Nicolás de los Garza, Nuevo León, México. E-mail: bkhariss@hotmail.com*

[b] *Department of Chemistry, Southern Federal University, 344090 Rostov-on-Don, Russian Federation*

DOI: 10.1016/j.mencom.2022.09.031

Zr^{IV} metal–organic framework based on terephthalic acid and 1,10-phenanthroline has been prepared by solvothermal method. The product represents an effective adsorbent for solid phase extraction of tetracycline antibiotics from aqueous media.



Keywords: adsorption, metal–organic frameworks, tetracycline, sorbent, solid phase extraction.

Zirconium-based metal–organic frameworks (Zr-MOFs) have drawn a lot of attention in analytical chemistry due to their promising adsorption properties, namely good selectivity, high productivity, low cost, regeneration ability and strong interaction of Zr–OH groups with the functionalities of pollutants.[1–5] Disadvantages of Zr-MOFs comprise low adsorption capacity and long equilibrium time. For an increase in the adsorption capacity, the mixed-ligand strategy is employed in the design of MOFs[6,7] including two organic ligands with similar or completely different types, *e.g.*, carboxyl group with its flexible coordination mode satisfying the coordinated configuration of a metal ion and a polypyridine organic ligand with its termination or chelation ability. Various ligands of the polypyridine type such as 2,2′-bipyridine or 1,10-phenanthroline are used together with carboxylate ions in the mixed-ligand approach to Zr-MOFs.[8–12]

In this work, we obtained a Zr-MOF based on terephthalic acid and 1,10-phenanthroline as well as used it for solid phase extraction (SPE) of tetracycline. Tetracycline antibiotics represent the broad spectrum ones active against both gram-positive and gram-negative bacteria. They are employed as food additives to prevent or treat mastitis and metritis in cows. However, the bioavailability of tetracycline in dairy cows is estimated to be 25–75%, so its significant amount passes into cow's milk and then affects human health.

The Zr-MOF sorbent was synthesized by solvothermal method using reaction of $ZrCl_4$, terephthalic acid and 1,10-phenanthroline in DMF† as well as characterized by IR spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and elemental analysis.‡ IR spectrum of the product after drying *in vacuo* at 60 °C [Figure 1(*a*)] reveals an intense and wide band at ~3400 cm^{-1} as an evidence of the presence of both crystallization and physically sorbed water inside the cavities of the compound. Drying the sample *in vacuo* at 150 °C resulted in a sharp decrease in the intensity of this band, so we considered these conditions as an activation mode. An intense doublet at 1589 and 1395 cm^{-1} is attributed to symmetric and antisymmetric vibrations of carboxylate ion. The main IR peaks are in good agreement with the coordination architecture of analogous compounds.[8–12] In the XRD profile [Figure 1(*b*)], the following peaks are distinguished: doublet 7.40 and 7.77, 9.38, 10.4, 13.14, 15.77, 17.44, 22.80, 23.45, 45.52 and 50.08°, which satisfactorily coincide with the ones calculated using Match-3 and PowderCell software. According to SEM image [Figure 1(*c*)], the substance is formed by the crystals of cubic shape having 4 μm edges with a background of immature and partially destroyed crystals, EDX data being in good agreement with elemental analysis.§

Considering the UV-VIS absorption spectrum of tetracycline in the range of 200–800 nm, the maximum at ~320 nm was set off and its intensity naturally decreased with the time of contact with the adsorbent. Therefore, to explore the adsorption dynamics of the synthesized complex we used this maximum.

For a 100 mg dm^{-3} tetracycline solution, an adsorption equilibrium was quickly achieved after immersing the sorbent in the solution for < 1 h [Figure 2(*a*)]. The adsorption activity for the sorbent at 10 °C was relatively low, while the adsorption at 20 and 35 °C proceeded with almost coinciding curves. Effect of ions such as Na^+, K^+, Ca^{2+}, Al^{3+}, Fe^{3+}, Cl^-, SO_4^{2-}, CO_3^{2-} and PO_4^{3-} coexisting in real wastewater on the tetracycline removal was also

† $ZrCl_4$ (2.33 g, 10 mmol) was dissolved in DMF (20 ml), then terephthalic acid (3.3 g, 20 mmol) dissolved in hot DMF (30 ml) and 1,10-phenanthroline (1.8 g, 10 mmol) in DMF (10 ml) were added. The resulting mixture was sealed in a glass ampoule, which was completely immersed in a vessel with fine calcined sand and heated at 132 °C for 72 h. After that the ampoule was opened, the resulting compound was filtered off, dried at 60 °C in air and activated by heating *in vacuo* at 150 °C for 8 h. Yield 3.52 g (83.2%). Found (%): C, 52.11; H, 2.65; N, 4.83; Zr, 22.1. Calc. for $Zr_2C_{56}O_{16}H_{32}N_4$ (%): C, 52.1; H, 2.5; N, 4.3; Zr, 21.18.

‡ SEM and EDX data were obtained using a LEO SUPRA 25 scanning electron microscope (Carl Zeiss). FT-IR spectra were recorded on a Varian 3100 Excalibur spectrometer using KBr pellets and the data analysis software from Spectra Soft Technologies. XRD analysis was carried out on an XR 4.0 diffractometer (PHYWE).

§ Found using EDX (%): C, 52.35; O, 19.68; N, 4.87; Zr, 21.27.

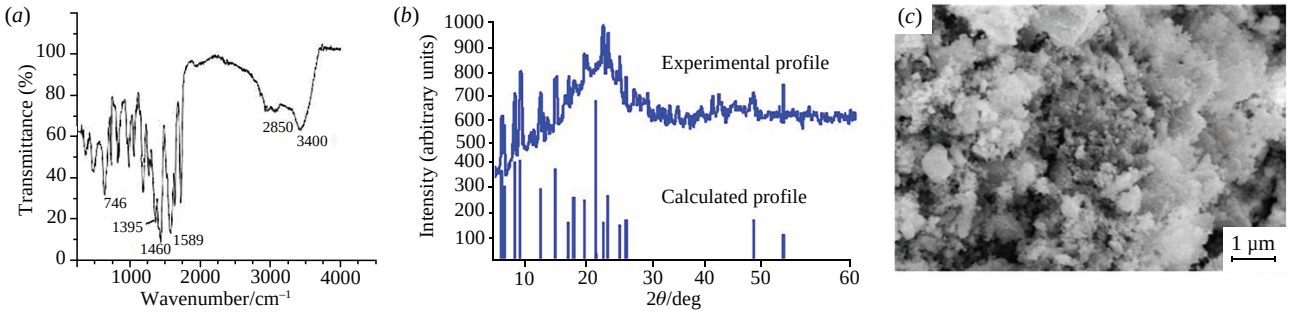


Figure 1 (*a*) IR spectrum, (*b*) XRD pattern and (*c*) SEM image of the sorbent synthesized.

investigated. As seen in Figure 2(*b*), the sorbent still retained high adsorption characteristics for tetracycline in an environment with multiple ions up to concentrations of 0.2 mol dm^{-3}, *i.e.*, kept 60–90% efficiency. With an increase in ionic strength of the solution, the sorption first decreases smoothly and then drops significantly. The elevated ionic strength leads to reduction of electrostatic attraction between the sorbent and the sorbate due to increased surface charge, which in turn lowers the adsorption. In addition, an elevated concentration of NaCl results in competition between Na^+ ions and tetracycline for the adsorption sites of MOF, while an increase in the amount of Cl^- ions contributes to the compression of pore size, which ultimately decreases sharply the sorption activity of the complex with respect to tetracycline.

Industrial wastewater containing tetracycline has different pH values, so it is important to explore the effect of pH on the adsorption. As reported,[13] tetracycline is unstable in a strong acid (pH < 2) or a strong base (pH > 10) medium. The adsorption capacity of MOF changed insignificantly with pH and had a maximum value at pH 4.5–7.5 [Figure 2(*c*)].

Taking into account the kinetics of adsorption as well, we can conclude that the high adsorption stability is attributed to the strong tetracycline–sorbent chemical interaction and the adsorption capacity is comparable to that of other sorbents.[14–19] The reason is unique skeletal stability of the Zr-based MOF material and the presence of active adsorption sites, which is important for the tetracycline removal.

Small concentrations of the sorbent have a relatively low efficiency, however, upon reaching 78 mg dm^{-3} an abrupt increase in adsorption activity occurs [Figure 3(*a*)]. The limiting value of adsorption is ~139.4 mg g^{-1}, which is quite a good indicator in comparison with published values of 24–36 mg g^{-1}. Thus, the new complex exhibits good adsorption activity for tetracycline in aqueous solution, even if the solution has a significant ionic strength. To understand the adsorption process, kinetics of the tetracycline adsorption was explored. Fitting the experimental data for the sorbent, we found that the pseudo-first kinetic model was highly consistent, indicating that the chemical adsorption played a significant role. The adsorption kinetic

Table 1 Thermodynamic parameters of tetracycline adsorption from aqueous solution.

T/K	ΔG^0/kJ mol^{-1}	ΔH^0/kJ mol^{-1}	ΔS^0/J mol^{-1} K^{-1}	*K*	*k*
283	–67.8				
291	–74.3	–62.5	18.8	1.02	0.0635
308	–81.64				

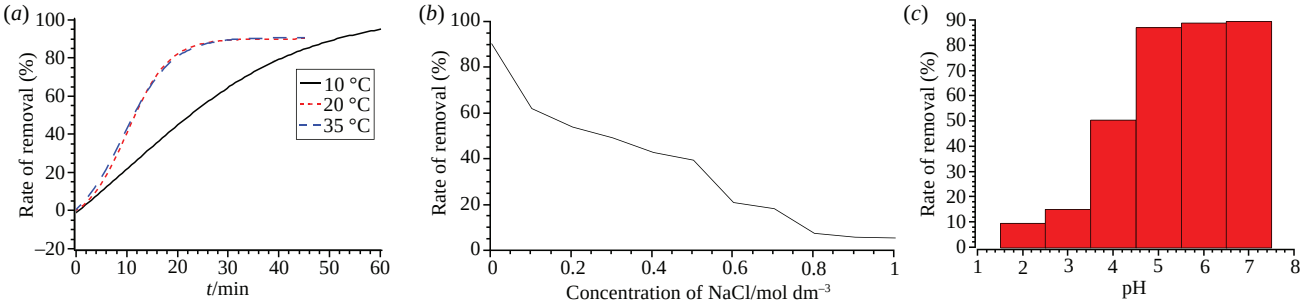


Figure 2 Tetracycline removal from aqueous solution as a function of (*a*) time, (*b*) concentration of NaCl and (*c*) pH.

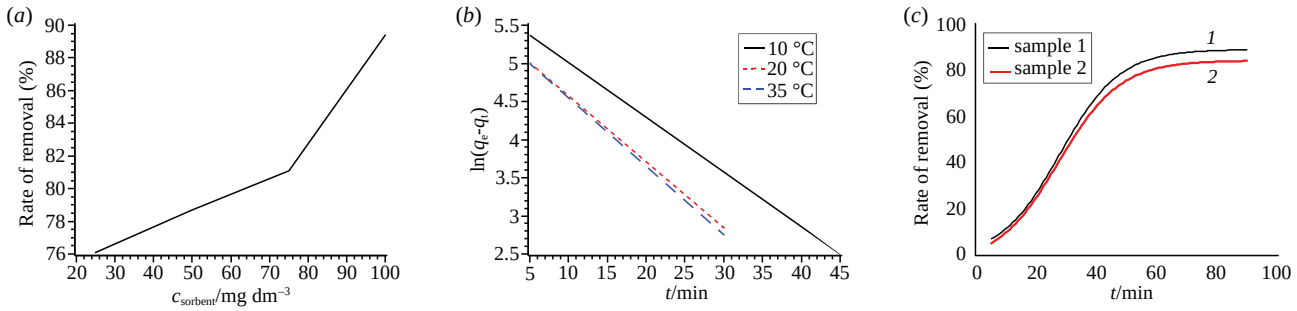


Figure 3 (*a*) Effect of sorbent concentration on the tetracycline removal from an aqueous solution, (*b*) tetracycline adsorption kinetic model and (*c*) efficiency of tetracycline removal from milk serum.

Table 2 Tetracycline removal from milk samples using SPE.

Milk sample	Tetracycline content before SPE/mg dm^{-3}	Tetracycline content after SPE/mg dm^{-3}	SPE efficiency (%)
From a private manufacturer, not heat-treated	< 0.001	Not determined	–
From a point of sale, pasteurized [Figure 3(*c*), sample 1]	0.005	0.00077	84.6
From a point of sale, sterilized [Figure 3(*c*), sample 2]	0.007	0.00124	82.3

curves at 20 and 35 °C are actually the same, while at 10 °C the velocity has significantly lower values [Figure 3(*b*)].

All the experimental data were fit using the Langmuir (L) and Freundlich (F) models, the following parameters of the approximating isotherms were obtained: K_L = 0.0357, R^2 = 0.9565 and K_F = 0.173, R^2 = 0.8961. The Langmuir model fits the adsorption isotherms better than the Freundlich one, indicating that tetracycline is adsorbed uniformly onto the MOF material and monolayer adsorption is the main interaction mechanism. The determined values of ΔG, ΔH and ΔS are given in Table 1, the enthalpy change of the adsorption process is negative, which indicates an exothermic process. The adsorption capacity decreases with an increase in temperature.

Then we attempted to analyze tetracycline in milk purchased from a retail outlet and in the market from a random seller, using the SPE with spectrophotometric detection. The calibration curve was linear for the concentration range 1.0–9.0 mg dm^{-3} with a correlation coefficient $R^2 > 0.9995$. The rate of tetracycline removal from a milk sample at initial antibiotic concentrations of 0.5, 1.0 and 2.0 mg dm^{-3} was determined, the average percent removal was found to be appropriate [Figure 3(*c*) and Table 2]. The limit of detection (LOD) and limit of quantification (LOQ) values for tetracycline were 0.03 and 0.1 mg dm^{-3}, respectively. The effectiveness of SPE of tetracycline from aqueous solution was slightly higher than from milk.

In summary, a new mixed-ligand Zr^{VI} MOF based on terephthalic acid and 1,10-phenanthroline was obtained by solvothermal method. The product purification avoids complicated and expensive washing as well as prolonged drying. The synthesized MOF represents an effective adsorbent for the removal of tetracycline from aqueous media and a real object like milk. The limiting value of adsorption is ~139.4 mg g^{-1}, which is quite a good indicator compared with the published values.

References

1 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.

2 O. V. Solovtsova, A. L. Pulin, I. E. Men'shchikov, N. P. Platonova, M. K. Knyazeva, S. S. Chugaev, A. V. Shkolin and A. A. Fomkin, *Prot. Met. Phys. Chem. Surf.*, 2020, **56**, 1114.

3 A. A. Pribylov, K. O. Murdmaa and O. V. Solovtsova, *Russ. Chem. Bull.*, 2021, **70**, 665.

4 Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327.

5 A. A. Chernyshev, D. N. Lytkina, A. S. Buiakov, S. N. Kulkov and I. A. Kurzina, *Mendeleev Commun.*, 2021, **31**, 881.

6 G. I. Dzhardimalieva and I. E. Uflyand, *RSC Adv.*, 2017, **7**, 42242.

7 Y. Yang, G. Ren, W. Li, D. Gu, Z. Liang, Y. Liu and Q. Pan, *Polyhedron*, 2020, **185**, 114599.

8 L. Dun, B. Zhang, J. Wang, H. Wang, X. Chen and C. Li, *Crystals*, 2020, **10**, 1105.

9 B.-P. Yang, H.-Y. Zeng, J.-G. Mao, G.-C. Guo, J.-S. Huang and Z.-C. Dong, *Transition Met. Chem.*, 2003, **28**, 600.

10 A. Chinthamreddy, R. Karreddula, G. K. Pitchika and M. S. SurendraBabu, *J. Inorg. Organomet. Polym. Mater.*, 2021, **31**, 1381.

11 H.-P. Xiao, Z. Shi, L.-G. Zhu, R.-R. Xu and W.-Q. Pang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2003, **59**, m82.

12 X.-L. Wang, Y.-F. Bi, H.-Y. Lin and G.-C. Liu, *Cryst. Growth Des.*, 2007, **7**, 1086.

13 Z.-h. Yang, J. Cao, Y.-p. Chen, X. Li, W.-p. Xiong, Y.-y. Zhou, C.-y. Zhou, R. Xu and Y.-r. Zhang, *Microporous Mesoporous Mater.*, 2019, **277**, 277.

14 *Pharmaceuticals in the Environment. Sources, Fate, Effects and Risks*, ed. K. Kümmerer, 3rd edn., Springer, 2008.

15 C. Du, Z. Zhang, G. Yu, H. Wu, H. Chen, L. Zhou, Y. Zhang, Y. Su, S. Tan, L. Yang, J. Song and S. Wang, *Chemosphere*, 2021, **272**, 129501.

16 N. Li, L. Zhou, X. Jin, G. Owens and Z. Chen, *J. Hazard. Mater.*, 2019, **366**, 563.

17 J. Jin, Z. Yang, W. Xiong, Y. Zhou, R. Xu, Y. Zhang, J. Cao, X. Li and C. Zhou, *Sci. Total Environ.*, 2019, **650**, 408.

18 Y. Dong, T. Hu, M. Pudukudy, H. Su, L. Jiang, S. Shan and Q. Jia, *Mater. Chem. Phys.*, 2020, **251**, 123060.

19 J. Yu, W. Xiong, X. Li, Z. Yang, J. Cao, M. Jia, R. Xu and Y. Zhang, *Microporous Mesoporous Mater.*, 2019, **290**, 109642.

Received: 9th March 2022; Com. 22/6820