Adsorption of Gatifloxacin from Aqueous Solution with Highly Stable Zr(IV)-Based Porphyrinic Metal-Organic Frameworks

Chen J.-J., Wang L.-J., Xu G.-J., Wang X.*, Zhao R.-S.

Key Laboratory for Applied Technology of Sophisticated Analytical Instruments of Shandong Province, Shandong Analysis and Test Center, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, China

* corresponding author: Xia Wang: e-mail: xia-w21cn0@163.com

Abstract

Water stable Zr-metal–organic framework nanoparticles (PCN-224 NPs) have been solvothermally synthesized. PCN-224 NPs show spherical shape with smooth surface and particle size of approximately 200 nm. PCN-224 NPs can be stable in acid and aqueous solutions, as confirmed by powder X-ray diffraction. Gatifloxacin (GTF) adsorption measurements showed that PCN-224 NPs exhibit a high adsorption capacity of 876 mg·g-1. Meanwhile, the adsorption factors, adsorption characteristics, and mechanisms of GTF were investigated in batch adsorption experiments.

Keywords: gatifloxacin; Zr(IV)-based porphyrinic metal-organic frameworks; adsorption

1. Introduction

With the rapid development of human technology, the residual amount of antibiotics continued to trend higher in ecological environment, especially the water environment (Zhou, L.J., etc.). Many studies have reported that there are a variety of antibiotics in waste water (Li W.H., etc., and Golovko, O., etc.), groundwater (Chen, K., etc. and Jiang, Y.H., etc.), and surface water (Watkinson, A.J., etc.).

As a new type of porous materials, metal-organic frameworks (MOFs) with excellent chemical and physical properties show of promising applications in various fields, especially those related to adsorption as solid phase microextraction (SPME) (Li, Q.L., etc.), and solid phase extraction (Tokalioglu, S., etc.).

In this paper, the Zr-MOFs (PCN-224) NPs (PCN stands for porous coordination network) was synthesized and applied in adsorption of gatifloxacin (GTF) in aqueous solution. Meanwhile the adsorption factors, characteristics and mechanism of a representative fluoroquinolone antibiotic, GTF, were investigated in detail.

2. Experimental

Zr-MOFs was synthesized (Park, J., etc.) and characterized by SEM, XRD, and TGA as shown in Figure 1.

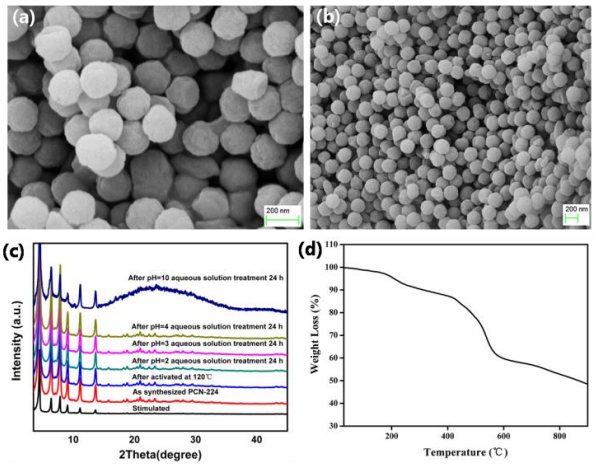

Figure 1. (a,b) SEM images,(c) XRD image and(d) TGA images of PCN-224NPs

3. Results and Discussion

3.1. Optimization of parameters of adsorption procedings

The performance of adsorbent is usually depicted by adsorption capacity and removal percentage. In the pre-experiment, the adsorption performance of PCN-224 NPs was excellent for GTF. 100% GTF were removed in 15 min when 10 mg PCN-224 powder was dispersed in 10 mL (80 mg·L^{-1}) GTF solution. Therefore, the effects of contract time, pH, and ionic strength on the adsorption of GTF onto PCN-224 NPs were investigated, and the results were shown in Figure 2.

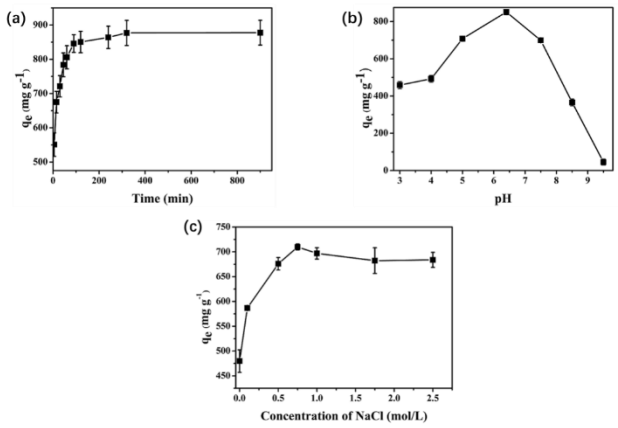

Figure 2. (a) Effect of contact time. (b) Effect of pH. (c) Effect of ionic strength.

3.2. Adsorption kinetics

To study the relationship between the structure of adsorbent and adsorption performance, the data in the adsorption equilibrium time experiment were used to fit the kinetic model. Four models were used to describe the adsorption process. The results were shown in Figure 3.

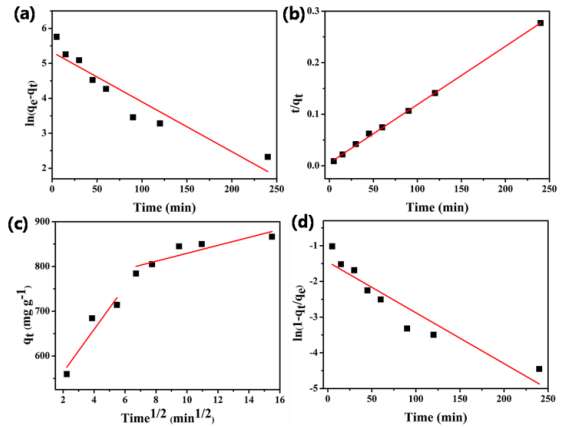

Figure 3. The kinetics models for adsorption of GTF on PCN-224 NPs: (a) pseudo-first-order model. (b) pseudo-second-order model. (c) intra-particle diffusion model. (d) liquid-film diffusion model.

4. Conclusions

In this study, Zr-MOF PCN-224 NPs were synthesized, and characterized. The adsorption performance and mechanism of PCN-224 NPs absorbing GTF from aqueous solution were also investigated. Various parameters such as contact time, pH and ionic strength were considered and optimized. The results show that the adsorption rate and removal percentage of GTF on PCN-224 NPs is quite high, and the adsorption kinetic fits the pseudo-second-order model better (R^2 = 0.999).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21477068 and 21777089), Key Research and Development Program of Shandong Province (2017GSF17107) and the Shandong Province Taishan Scholar Program (Jin-Ming Lin).

References

Zhou, L. J.; Ying, G. G.; Liu, S.; Zhao, J. L.; Yang, B.; Chen, Z. F.; Lai, H. J. (2013), Occurrence and fate of eleven classes of antibiotics in two typical wastewater treatment plants in South China. *Sci. Total Environ.* pp. 365-376.

Li, W. H.; Shi, Y. L.; Gao, L. H.; Liu J. M.; Cai, Y. Q. (2013), Occurrence and removal of antibiotics in a municipal wastewater reclamation plant in Beijing, *China. Chemosphere.* 92, 435-444.

Golovko, O.; Kumar, V.; Fedorova, G.; Randak, T.; Grabic, R. (2014), Seasonal changes in antibiotics, antidepressants/psychiatric drugs, antihistamines and lipid regulators in a wastewater treatment plant. *Chemosphere.* 111, 418-426.

Chen, K.; Zhou, J. L. (2014), Occurrence and behavior of antibiotics in water and sediments from the Huangpu River, Shanghai, *China. Chemosphere.* 95, 604-612.

Jiang, Y. H.; Li, M. X.; Guo, C. S.; An, D.; Xu, J.; Zhang, Y.; Xi, B. D. (2014), Distribution and ecological risk of antibiotics in a typical effluent receiving river (Wangyang River) in north *China. Chemosphere.* 112, 267-274.

Watkinson, A. J.; Murby, E. J.; Kolpine, D. W.; Costanzo, S. D. (2009), The occurrence of antibiotics in an urban watershed: From wastewater to drinking water. *Sci. Total Environ*. 407, 2711-2723.

Li, Q. L.; Wang, X.; Chen, X. F.; Wang, M. L.; Zhao, R. S. (2015), In situ hydrothermal growth of ytterbium-based metal-organic framework on stainless steel wire for solid-phasemicroextraction of polycyclic aromatic hydrocarbons from environmental samples. *J. Chromatogr. A.* 1415, 11-19.

Tokalıoglu, S.; Yavuz, E.; Selçuk D.; Patat, S. (2017), Zirconium-based highly porous metal-organic framework (MOF-545) as an efficient adsorbent for vortex assisted-solid phase extraction of lead from cereal, beverage and water samples. *Food Chem.* 237, 707-715.

Park. J.; Jiang, Q.; Feng, D. W.; Mao, L. Q.; Zhou, H. C. (2016), Size-Controlled Synthesis of Porphyrinic Metal−Organic Framework and Functionalization for Targeted Photodynamic Therapy. *J. Am. Chem. Soc.* 138, 3518-3525.