

Selective Removal and Degradation of Ciprofloxacin Bearing Wastewater by HKUST-1

Divya Dixit¹, Sudipta Sarkar¹

¹ Indian Institute of Technology Roorkee
Roorkee, India

ddixit@ce.iitr.ac.in; sudipta.sarkar@ce.iitr.ac.in

The current sewage treatment cannot remove many emerging contaminants, including antibiotics which at tiny concentrations can give rise to antimicrobial resistance (AMR) in the bacteria. Several researchers have pointed out that most such AMR bacteria (ARB) get produced at sewage treatment plants (STPs). Due to conducive growth conditions, there is a natural selection of ARBs resulting in selective proliferation [2]. The STPs generally do not practice rigorous disinfection of the treated wastewater to avoid the generation of disinfection by-products. Thus, there is a high risk of the spread of ARBs from the STPs, thus posing a potential public health threat. Therefore, it is required to prevent the development of ARBs within the STPs. The fundamental working principle of the STPs involves providing conducive conditions for the exponential growth of microbes that degrade the organic matter in the wastewater. Tiny concentrations of antibiotics and favorable growth conditions cause natural selection and proliferation of ARBs. Thus, the only strategy to check the growth of ARB in STPs is to remove the antibiotics before the sewage enters the biological treatment unit of the STP. Efficient treatment requires selective removal and selective destruction of trace concentrations of antibiotic residues from the background of overwhelmingly high concentrations of organic matter, which is a difficult task. Currently, all remediation technologies either target treating treated wastewater post-biological unit or lack selectivity and thus are cost-prohibitive [3,4]. In this study, the idea is to develop a highly effective process for the selective degradation of antibiotic ciprofloxacin from the background of high concentrations of organic matter, i.e., wastewater entering the STPs[1].

Fundamentally, the method combines highly selective adsorption of ciprofloxacin by metal organic framework HKUST-1 followed by the destruction of the ciprofloxacin by advanced oxidation process (AOP). HKUST-1 was synthesized by the solvothermal method, and FTIR, XRD, and EDX-SEM analysis confirmed its structural properties. The antibiotic selected for the study, i.e., ciprofloxacin, has dissociation constants pKa1 and pKa2 as 6.1 and 8.7. At pH less than 6.1, protonation of the amine group occurs in piperazine moiety; thus, ciprofloxacin mainly exists as cations. Also, at a pH greater than 8.7, ciprofloxacin molecules behave as anions due to the loss of protons from the carboxylic group. The adsorption capacity of HKUST-1 came out to be 61.6 mg/g with the following reaction conditions : [ciprofloxacin]= 1ppm, pH 8, reaction volume =200 ml, [Hkust-1]= 10mg, time=40 minutes. Premodified (with a photocatalyst i.e. TiO₂ HKUST-1 mineralized the target compound ciprofloxacin under UV light within 15 minutes, and the catalyst was regenerated for different cycles.

The adsorbent HKUST-1 and the target antibiotic molecules (ciprofloxacin) are held by more than two interactions, namely electrostatic (ion exchange), hydrophobic, and Lewis acid-base interactions, thus giving rise to immense selectivity. Given the novelty of the process, cost-effectiveness, and the need of the hour, the material and process would find commercial success when realized.

References

- [1] T. J. Al-Musawi, A. H. Mahvi, A. D. Khatibi, & D. Balarak, "Effective adsorption of ciprofloxacin antibiotic using powdered activated carbon magnetized by iron(III) oxide magnetic nanoparticles," *J. of Por. Mat.*, vol 28, no.3, 835–852,2021.
- [2] Y. Cai, T. Sun, G. Li, & T. An, "Traditional and Emerging Water Disinfection Technologies Challenging the Control of Antibiotic-Resistant Bacteria and Antibiotic Resistance Genes" *ACS ES&T Engineering*, vol. 1. no. 7, 1046–1064,2021.

- [3] Osińska, M. Harnisz, E. Korzeniewska, “Prevalence of plasmid-mediated multidrug resistance determinants in fluoroquinolone-resistant bacteria isolated from sewage and surface water” *Env. Sci. and Pol. Res.*, vol. 23, no. 11, 10818–10831, 2016.
- [4] Y. Wang, L. Zhang, “Improved performance of 3D hierarchical NiAl-LDHs micro-flowers via a surface anchored ZIF-8 for rapid multiple-pollutants simultaneous removal and residues monitoring”, *J. of Haz. Mat.*, vol. 39, no. 5, 2020.