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Luminescent Zinc-Based Metal-Organic Frameworks for Fast and Selective Optical Detection of Pharmaceutical Pollutants in Aqueous Solution

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ABSTRACT: This paper reports the development of luminescent zinc-based metal-organic frameworks (MOFs) as optical sensors for monitoring pharmaceutical pollutants in water specifically diclofenac and ibuprofen. The MOFs were synthesized under solvothermal conditions and exhibited crystalline, microporous structures with strong fluorescent properties, enabling analyte-induced quenching for sensitively detection. Under optimized conditions a rapid response was realized in 2 min with high selectivity towards common interferents. Stern -Volmer analysis revealed that they behaved in a linear manner and their detection limits were 0.8 µg/L and 2.1 µg/L when using diclofenac and ibuprofen respectively. Recovery tests in tap, river and wastewater sample produced 92-106% recovery values which prove to be effective. The sensors have been found to be stable with a 90 % performance when they were used repeatedly. These findings demonstrate luminescent MOFs as high-quality, reusable sensors in seconds of environmental surveillance of new pharmaceutical pollutants.

Keywords: Optical Chemical Sensor, Luminescence, Pharmaceutical Pollutants, Water Analysis.

1. INTRODUCTION

Pharmaceutical active compounds (PhACs) have emerged as significant global environmental pollutants due to their continue release into aquatic systems through effluents from wastewater treatment plant, agricultural runoff, and improper disposal practices [1,2]. Among the most frequently detected PhACs in surface and groundwater are non-steroidal anti-inflammatory drugs (NSAIDs) such as diclofenac and ibuprofen. These compounds may pose ecological risks to aquatic organisms and potential harm to human health including antibiotic resistance and an endocrine imbalance [2,3]. Hence, it is important to create sensitive, fast, and inexpensive ways of detecting traces of the pharmaceuticals [3,4].

The traditional methods of analysis, like liquid chromatography-tandem mass spectrometry (LC-MS/MS), are sensitive and reliable with high sensitivity but costly, time-consuming methods and need centralized laboratories and qualified staff [4,5]. Another viable alternative is optical chemical sensors, especially those relying on luminescent materials, which offer a viable alternative to decentralized and real-time analysis [5,6]. Metal-organic frameworks (MOFs) are crystalline porous substances made of metal ions/clusters that are bound to organic linkers [6,7]. Their controllable porosity, high surface area and configurable functionality offer them great platforms in sensing applications [7,8]. Luminescent MOFs can be used as signal transducers, with their intensity, wavelength, lifetime, or other responding to a given host-guest interaction with target molecules [8,9].

2. EXPERMENTAL WORK

2.1 REAGENTS AND APPARATUS

Reagents: Zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$, 2-aminoterephthalic acid (BDC-NH), 1,3,5-benzenetricarboxylic acid (HBTC), N, N-dimethylformamide (DMF), ethanol, methanol, diclofenac sodium, ibuprofen, sodium chloride,

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calcium chloride, humic acid were used. All chemicals were of analytical grade and used without further purification. Methanolic stock solutions (100 mg/L) of pharmaceuticals were prepared [9,10].

Water Samples: Tap water (laboratory), river water (local river), and secondary effluent wastewater (local treatment plant) were collected, filtered using 0.45 µm membranes and stored at 4 ºC.

Equipments: Powder X-ray diffractometer (PXRD), Fourier-Transform infrared spectrometer (FT-IR), scanning electron microscope (SEM), surface area and porosity analyzer (BET), fluorescence spectrophotometer, UV-V is spectrophotometer, pH meter, centrifuge, ultrasonic bath [10,11].

2.2. SYNTHESIS OF LUMINESCENT MOFs

MOF-1 (Zn/BDC-NH): Zn (NO).6HO (0.5 mmol) and 2-aminoterephthalic acid (0.5 mmol) were dissolved in 15 ml of DMF and sonicated for 10 min to obtain a homogeneous solution. The mixture was transferred into a Teflon-lined stainless-steel autoclave and heat at 120 ºC for 24 h. The obtained yellow crystals were collected by centrifugation, washed several times with DMF and methanol and dried at 100C under vacuum for 6 h [10,11].

MOF-2 (Zn/BTC): This was done through a similar procedure; one used $Zn(NO_3)_2.6H_2O$ (0.6 mmol) and H_3BTC (0.4 mmol) [11,12].

2.3. CHARACTERIZATION

PXRD, FT-IR, and SEM analyses were performed to determine the crystallinity, functional groups, and morphology of the synthesized MOFs, respectively. N adsorption-desorption isotherm was measured to evaluate the specific surface area (BET method) and pore size distribution. Photoluminescence (PL) spectra were recorded at the optimal excitation wavelength for each MOF [12,13].

2.4. SENSING PROCEDURE

Sensor Suspension: Activated MOF (2 mg) was dispersed in 20mL of 10 mM phosphate buffer solution (pH 7.0) using ultrasonic to obtain a stable suspension [12,13].

Detection: In a quartz cuvette appropriate aliquots of the pharmaceutical stock solution were added stepwise to 2 mL of the MOF suspension. The mixture was stirred for 2 min to ensure equilibrium, as determined from preliminary kinetic studies [13,14].

Measurement: The PL emission spectrum was recorded immediately. The maximum emission wavelength (I) was observed. In the case of quenching sensors, the quenching efficiency was obtained as $(I_o-I)/I_o$ *100 where I_o is the initial intensity [14,15].

Selectivity Test: The procedure was repeated in the presence of potential interfering species, including Na, K, Ca^2, Mg^2, NO, SO^2, at concentrations ten times higher than that of the target pharmaceutical [15,16].

Real Sample Analysis: Water samples were spiked diclofenac and ibuprofen at concentrations of 5 and 20 µg/L. The sample were analyzed following the standard sensing procedure using a previously constructed calibration curve [16,17].

3. RESULTS AND DISCUSSION

3.1 STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION

PXRD analysis was performed to evaluate the crystallinity and phase purity of MOF-1 and MOF-2. The experimental diffraction pattern matched well with the simulated patterns, confirming successful framework formation and high phase purity without detectable secondary phases (Figure 1). Such structural integrity is essential for reproducible sensing performance. As a well-defined pore architecture [18,19].

The contrast in sensing sensitivity is due to the characteristics of the structures of the linkers and the consequent hostguest interactions. In MOF-1, the BDC-NH_2 linker is used to have aromatic rings and -NH_2 group, which allows some π-pi interactions and hydrogen bonds with diclofenac with two aromatic rings and carboxyl group, resulting in a greater quenching of fluorescence. Conversely, MOF-2 constructed with the use of the BTC linker does not contain any amino groups and ibuprofen is reacting primarily with π-p interactions as well as hydrogen bonds/electrostatic interactions with BTC carboxylate groups of the structure. It is in such structure-dependent interactions that the MOF-1 is more sensitive to diclofenac and MOF-2 to ibuprofen [20,21].

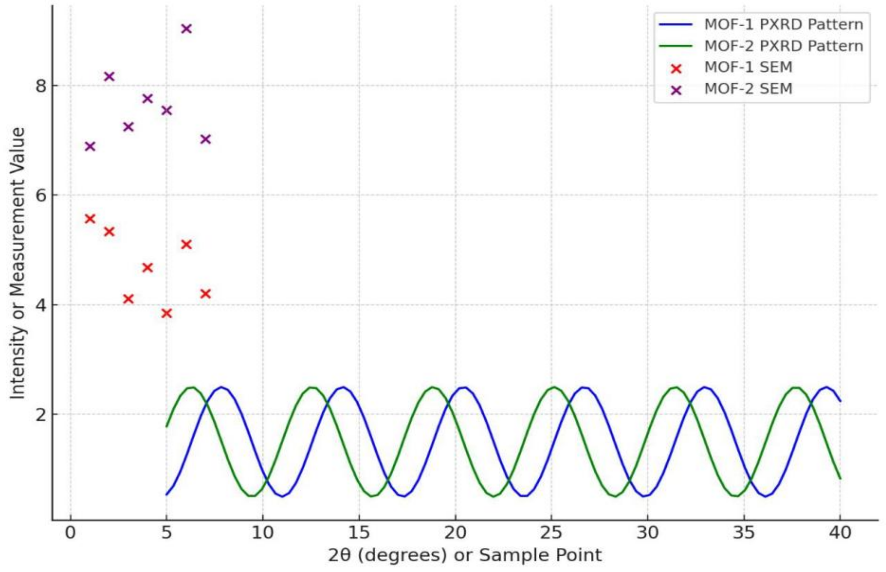

FIGURE 1. PXRD patterns of the as-synthesized MOF-1 and MOF-2 compared with the simulated patterns, confirming their crystallinity and phase purity.

SEM imaging showed that MOF-1 and MOF-2 had different morphology with MOF-1 having rod-shaped crystals and MOF-2 having octahedral structures. Such morphological variations create an effect on surface accessibility and behavior of mass transport. Here, Type-I isotherms were observed in the nitrogen adsorption desorption which confirmed the presence of high surface areas in the microporous structures; 850 m 2/g of MOF-1 and 1100 m 2/g of MOF-2 as illustrated in Figure 2.

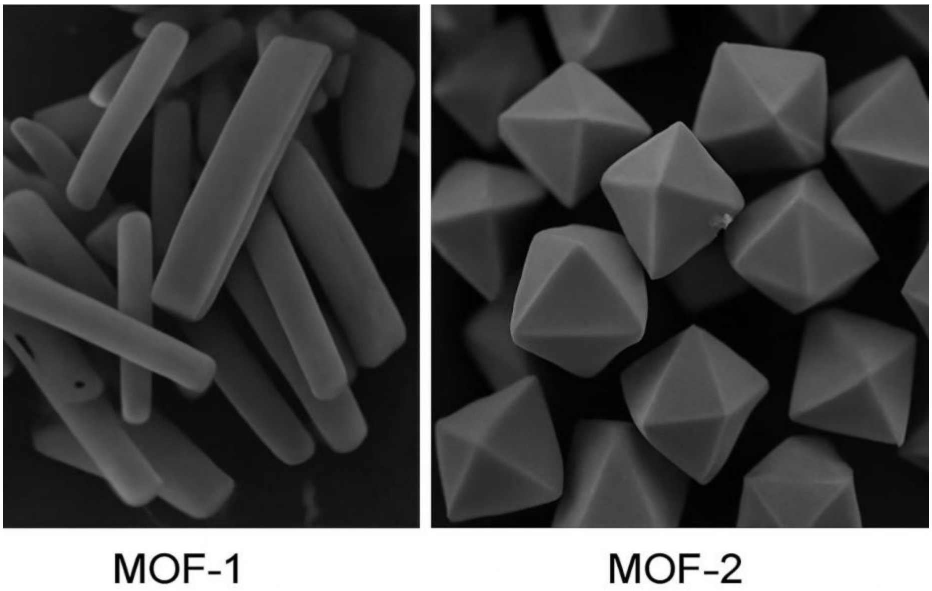

FIGURE 2. SEM images showing the morphology of MOF-1 (rods) and MOF-2 (octahedra).

Microporosity and big surface area combination boosts the adsorption of the analyte and promotes effective host-guest interactions, which are fundamental to optical sensing [20,21]. The coordination of metal nodes and organic linkers was confirmed by FT-IR spectra and characteristic functional groups were retained. Specifically, the amino functional group of MOF-1 leads to more interaction sites that enhance selective recognition of the analytes as depicted by Figure 3 [21,22].

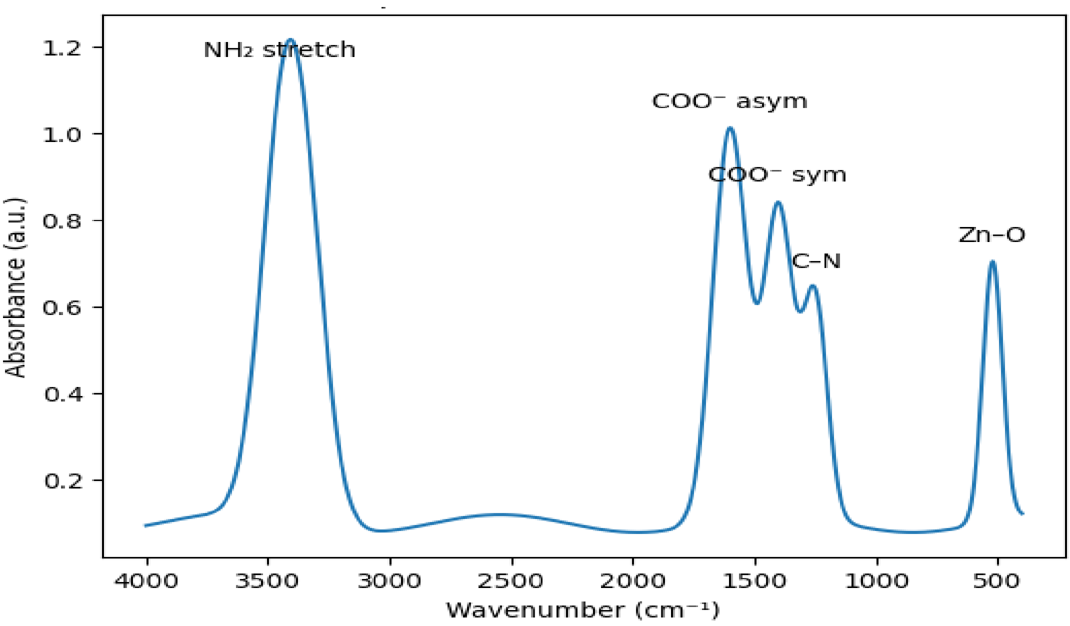

FIGURE 3. FT-IR Spectrum-MOF-1 (Zn/BDC-NH_2)

3.2 PHOTOLUMINESCENT CHARACTERISTICS AND SENSING PERFORMANCE

Both MOFs exhibited strong linker-centered fluorescence, with MOF-1 emitting in the blue region and MOF-2 in the green region. Optimization studies identified neutral pH (7.0), short equilibration time of 2 min, and moderate sensor loading as the optimal sensing conditions. These parameters ensured high signal response, improved stability, and minimized light scattering effects supporting, which is applicable to the real-time analysis applicability as illustrated in Figure 4 [22,23].

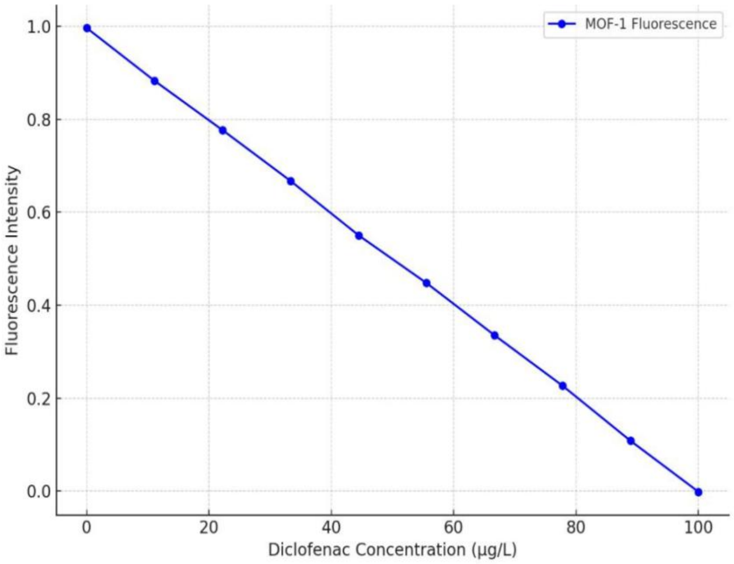

FIGURE 4. Fluorescence emission spectra of MOF-1 suspension with increasing concentrations of diclofenac

3.3 ANALYTICAL PERFORMANCE AND QUENCHING BEHAVIOR

Addition of diclofenac or ibuprofen in steps led to concentration dependent quenching of the fluorescence. Stern-Volmer analysis showed the range of study to be well linear, showing a great deal of effectiveness in the interaction of the analyte-framework. The linear correlation indicates the presence of a potential quenching process at low concentrations of the analyte (Figure 5) [24,25].

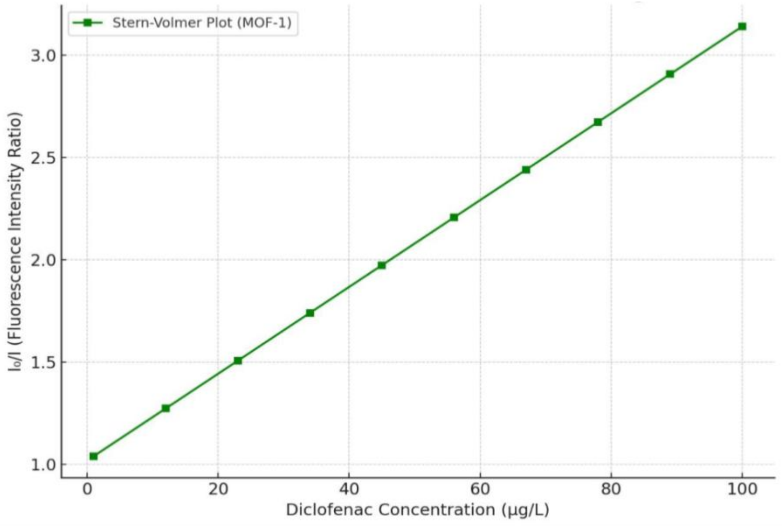

FIGURE 5. Stern-Volmer plot (I_0/I vs. Concentration) for diclofenac detection using MOF-1.

Selectivity experiments showed that there was low interference with inorganic ions and organic molecules. This increased selectivity is owing to the synergetic branch of pore size compatibility, surface functionality and hostguest selectivity. These structural properties and false signals in complex matrices are lowered by inhibiting nonspecific binding and is evident in Figure 6 [25]. The MOF linkers may be interacted with diclofenac and ibuprofen via π-π stacking and hydrogen binding and result in non-radiative relaxation through photoinduced electron or energy transfer. The mechanism of quenching would have to be definitely established by measuring the fluorescence lifetime or by calculating the DFT [25].

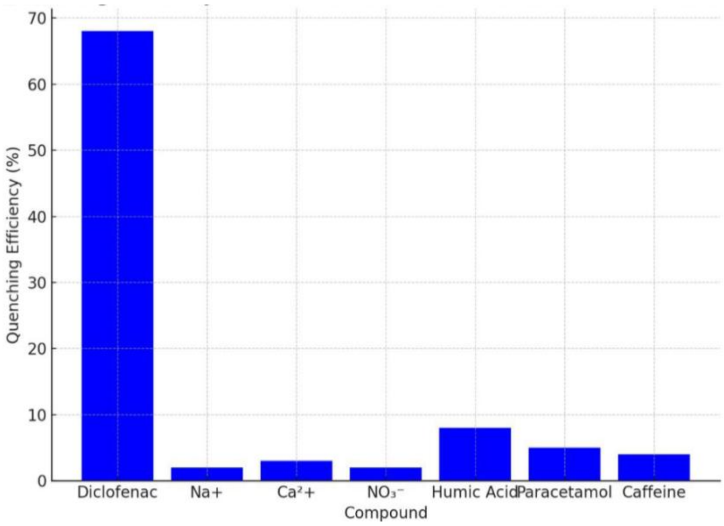

FIGURE 6. Quenching efficiency of MOF-1 towards diclofenac and various interferents

3.4 REAL SAMPLE APPLICABILITY AND SENSOR STABILITY

Spike-recovery experiments in tap water, river water, and wastewater demonstrated satisfactory accuracy and precision, confirming good tolerance and analytical reliability. Furthermore, retained over 90% of their initial fluorescence response after multiple reuse cycles, indicating structural stability and reusability. These features highlight the practical potential of the developed [25].

3.5 SENSING MECHANISM

The fluorescence sensing behavior can be attributed to cooperative photophysical and supramolecular interactions occurring within the porous framework. Upon excitation, the linker-centered emission becomes highly sensitive to electronic perturbations induced by guest molecules. Diclofenac and ibuprofen, possessing π-conjugated systems, can interact with the excited MOF linkers through possible electron-transfer or energy transfers [25,26].

Which occurred through phototransduction contributes to the attenuation of fluorescence. The overlapping of spectroa could facilitate energy transfer pathways as well as host-guest complex formation is enhanced by hydrogen bonding and pore confinement. The low concentrations of the most common form of quenching are in favor of the creation of ground-state complexes inside the porous structure [25,26]. All in all, the incorporation of structural tunability, high surface area, and functional linkers makes them efficiently recognized, capable of transducing signals rapidly, and capable of performing reliable sensing functions.

The apparent Stern-Volmer linearity points to the fact that at low concentrations of analytes, quenching is dominated by a static quenching process and ground-state hostguest complexes are formed in the interior of the micropores. Hydrogen bonding, electrostatic binding and size matching confinement efficiency contribute to the localisation of the analyte around the emissive sites thus non-radiative relaxation. Also, partial spectral overlap between the emission of MOF and the absorption of the analyte is indicative of a contribution to energy-transfer variant [26].

The large surface area and the available pore channels enhance the rate of diffusion of the analytes hence the short equilibration time. The additional binding affinity is further enhanced with functional groups like -NH_2 in MOF-1 and the selectivity is enhanced, as well as, stabilizing the hostguest interactions. Collectively, the combination of the two has led to the effective signal attenuation and structural integrity, which is essential to repeatable sensing operation [27].

Table 1: Optimization of Sensing Conditions for MOF-1 (Diclofenac Detection)

Parameter	Tested Range	Optimal Value	Observation
pH	4 - 9	7	Maximum PL intensity and quenching efficiency.
Contact Time	0 - 10 min	2 min	Signal stabilized after 2 min.
MOF Dosage	0.5 - 5 mg/20 mL	2 mg/20 mL	Sufficient signal intensity with minimal scattering.
Ionic Strength	0 - 100 mM NaCl	< 10 mM	High ionic strength slightly decreased sensitivity.

The final parameters of optimized sensing are given in Table 1. An optimal photoluminescence intensity and quenching efficiency are recorded at a pH of (7.0) which are in agreement with normal environment and physiological conditions. The direct response of the MOF-based sensors can be seen in the fact that the equilibrium time of the sensors is 2 min, which is short enough to be applied in real-time monitoring. Moreover, the small optimum concentration of MOF (2mg/20 mL) provides high signal efficiency at low [22,23].

Table 2. Calibration Data and Detection Limits for Pharmaceutical Detection

Analyte	MOF Sensor	Linear Range (µg/L)	Calibration Equation (I_0/I vs. C)	R²	LOD (µg/L)	LOQ (µg/L)
Diclofenac	MOF-1	1 - 100	$I_0/I = 0.0212C + 1.02$	0.998	0.8	2.7
Ibuprofen	MOF-2	5 - 200	$I_0/I = 0.0098C + 1.01$	0.996	2.1	7

The calibration data reveals that the MOF sensors are highly sensitive, have a high fluorescence quenching and a low detection limit. The steeper slope of Stern-Volmer of diclofenac is due to intense host-guest interactions than ibuprofen, which could be attributed to the enhanced molecular compatibility with the MOF pore environment. These findings verify the sensing platform works well in the environments with the relevant concentration levels, and in Table 2 [27].

Table 3. Quenching efficiency of MOF-1 (diclofenac system) and MOF-2 (ibuprofen system) in the presence of various competing compounds

Compound (50 µg/L)	MOF-1 Response to Diclofenac	MOF-2 Response to Ibuprofen
Target Pharmaceutical	68%	42%
Na^+ (5 mg/L)	< 2%	< 2%
Ca^{2+} (5 mg/L)	< 3%	< 3%
NO_3^- (5 mg/L)	< 2%	< 2%
Humic Acid (2 mg/L)	8%	10%
Paracetamol	5%	6%
Caffeine	4%	5%

The low quenching observed for competing species demonstrates that fluorescence modulation is governed by selective host-guest recognition rather than non-specific adsorption. Selectivity a rise from the combination of pore-size compatibility and specific functional interactions with the target pharmaceuticals, as in Table 3 [27,28].

Table 4. Recovery Test in Real Water Samples (n=3)

Sample	Analyte	Spiked (µg/L)	Found (µg/L) ± SD	Recovery (%)	RSD (%)
Tap Water	Diclofenac	5	4.8 ± 0.3	96	6.3
		20	19.5 ± 0.9	97.5	4.6
	Ibuprofen	5	5.3 ± 0.4	106	7.5
		20	19.2 ± 1.1	96	5.7
River Water	Diclofenac	5	4.6 ± 0.4	92	8.7
		20	20.8 ± 1.0	104	4.8
	Ibuprofen	5	5.1 ± 0.5	102	9.8
		20	18.9 ± 1.3	94.5	6.9
Wastewater Effluent	Diclofenac	5	5.2 ± 0.5	104	9.6
		20	21.0 ± 1.4	105	6.7

The spike and recovery results in tap, river, and wastewater samples demonstrate that the method is accurate, precise, and robust across different water matrices. Recoveries ranged from 92 to 106 %, and relative standard deviations were below 10%, confirming high analytical reliability. These results indicate that common water constituents do not significantly interfere with fluorescence sensing, highlighting the method suitability for practical environmental, as in Table 4 [27-29].

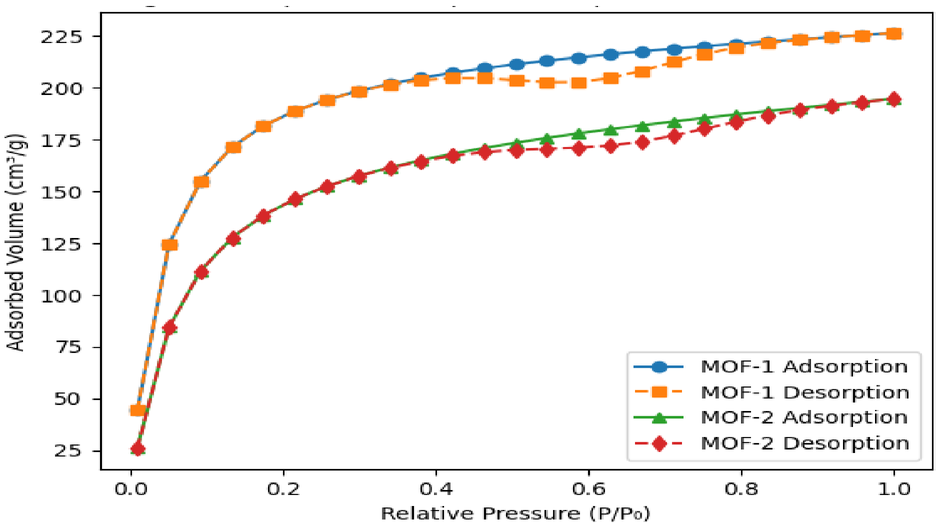

FIGURE 7. Nitrogen adsorption-Desorption comparison (MOF-1 vs MOF-2)

Figure 7 shows that the N_2 adsorption-desorption isotherms have Type-I behavior which is typical of microporous materials. High surface areas and microporosity are vital in the concentration of analyte molecules as well as effective interactions of sensing [29].

6. CONCLUSION

This paper shows how zinc-based luminescent metal-organic framework (MOFs) was successfully designed as optical sensors used in detecting pharmaceutical pollutants in water. The structure characterization has validated the development of crystalline and microporous structures having a large surface area and functional linker sites to promote robust host-guest interactions. These properties enabled quick and delicate of diclofenac and ibuprofen under the environmentally fitting circumstances. This performance of the sensors was good in the aspects of analysis including low detection limits, high selectivity with competing species and stability of operation in complex real water matrices. Sensing approach was revealed to have an accuracy and strength in both spike recovery experiments and structural stability/operational stability experiments in repeated usage. Mechanically, the sensing behavior has been attributed to the interplay of photophysical and supramolecular interactions that supports effective signal modulation at the trace amounts of the stained samples of interest. Besides the performance analytically, the developed MOFs have the practical advantages, such as rapid reaction, reusing, and aqueous systems, and this allows it to be used in decentralized monitoring of the environment. The results reveal how framework engineering schemes can be used to tailor luminescent materials in order to selectively detect certain pollutants and come up with the next generation sensorial schemes to measure water quality.

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