Functionalized MOF as a Sensitive Spectroscopic Probe for Hg²⁺, Co²⁺, and Al³⁺ Ions Detection in Aqueous Media

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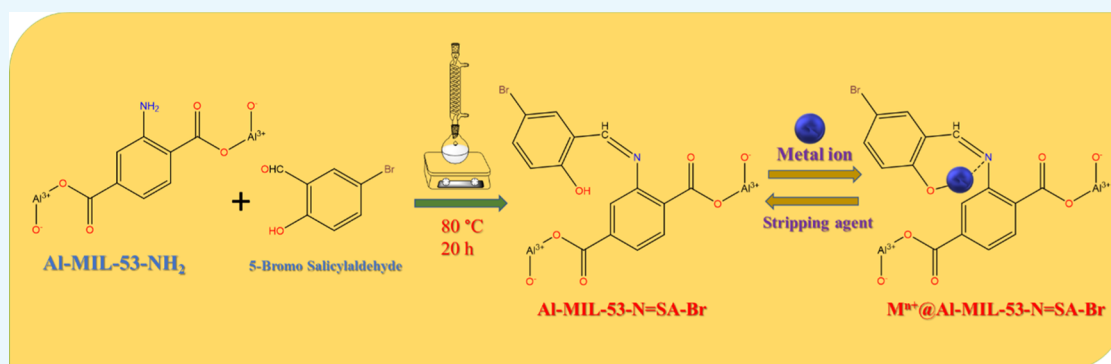
ABSTRACT: A modified metal−organic framework (MOF) named Al-MIL-53-N═SA-Br was synthesized via a Schiff-base reaction between the MOFs (Al-MIL-53-NH₂) and 5-bromo salicylaldehyde. The robust functionalized Al-MIL-53-N═SA-Br was used as a novel spectrophotometric sensor for detecting Hg²⁺, Co²⁺, and Al³⁺ ions. In a wide range of concentrations, the absorption spectral intensity of Al-MIL-53-N═SA-Br increased linearly upon increasing the concentration of Hg²⁺, Co²⁺, and Al³⁺ ions. The limit of detection (LOD) of the proposed Al-MIL-53-N═SA-Br sensor reached 1.52 ppm of Hg²⁺ ion (7.56×10^{-9} M). Therefore, this study introduces a novel ratiometric Hg²⁺, Co²⁺, and Al³⁺ ions chemosensor. Simple treatment using thiourea or ethylenediaminetetraacetic acid can remove the metal ions from the used sensor and use it many times with a high efficiency. In addition, the Al-MIL-53-N═SA-Br sensor has a high adsorption capacity for these metal ions. The design of the robust Al-MIL-53-N═SA-Br sensor provided high stability, reproducibility, selectivity, high sensitivity, and a facile sensing design. Furthermore, the good absorption spectral stability of Al-MIL-53-N═SA-Br in aqueous media, the broad linear in sensing, and the low LOD of the Hg²⁺, Co²⁺, and Al³⁺ ions show its high potential in determining these ions in real water.

INTRODUCTION

Heavy metal pollution is one of the most important challenges throughout the world in recent years, as city expansion and industries have increased. Environmental toxins have gotten a lot of attention since they may build up in the body of the human over time via the food chain, causing illnesses and difficulties. Some heavy metals, such as manganese, cobalt, copper, and zinc, are essential for living organisms, but extreme doses can be harmful.[1,2]

Mercury is ejected into the atmosphere naturally through volcanic explosions, earthquakes, and leakage from the earth's crust, among other things. Mercury may also be present in the form of mercury compounds, which are manufactured for industrial uses, either directly or indirectly, and practically everyone is exposed to it.[3] Mercury and its salts have been employed in medicinal purposes, such as laxatives since ancient times, skin ointments, diuretics, and antiseptics. In addition, it is still commonly utilized in amalgam dental fillings today. Mercury exposure has been correlated to a variety of health problems, such as neurological symptoms, kidney and brain

damage, and hormonal and immunological alterations, according to several pieces of research.[4] Because mercury has a high sensitivity to the neurological system, it can produce hallucinations, altered awareness, and other permanent life-threatening effects.[5]

Because it is an essential component of the vitamin B12 complex and the major metallic component of thiamine, cobalt plays a significant role in a variety of physiological activities. High levels of cobalt in the human body, on the other hand, can impair heart muscles, produce an overproduction of red blood cells, irritate the lungs, induce bone abnormalities, and hurt the thyroid gland.[6,7] Furthermore, a lack of cobalt in the

human body can result in severe retardation, anorexia, and megaloblastic anemia.[6] As a result, there is a growing interest and need for a cost-effective, quick, easy, and sensitive approach for detecting metals in environmental samples.

Aluminum is a common metal that causes both biotoxicity and phytotoxicity. Furthermore, aluminum is detrimental to plant growth as a result of its rapid restriction on root growth and significant unfavorable impacts on nutrient uptake.[8] Aluminum has been reported to affect the blood−brain barrier since it is simply absorbed by the central nervous system and accumulates in the brain under normal physiological settings.[9] As a result, aluminum poses a serious public health risk, as it may induce memory loss and cognitive impairment, leading to neurotoxic disorders, such as Parkinson's disease and Alzheimer's disease.[10] As a result, the amount of Al^{3+} ions in drinking water and surface water is strictly controlled by the Environmental Protection Agency (EPA).[11]

As a result, establishing a detection technique for these metals with a high selectivity and sensitivity is critical for the environment and human health, as they can pose serious threats to the human health and the ecosystem. To date, a variety of procedures for determining these metals have been published, including spectroscopy, high-performance liquid chromatography, atomic absorption spectroscopy, neutron activation analysis, and inductively coupled plasma (ICP) mass spectrometry. Because of its particular features, such as low cost, easy detection, fast reaction time, and high sensitivity, the spectrophotometric method is the highly appealing methodology utilized to detect low analyte concentrations among the detection methods.[12] Regardless, a variety of chemosensors have been described in order to detect these metals; ratiometric and spectrophotometric sensors are still under development.

During the previous two decades, a type of very porous material, metal−organic frameworks (MOFs), has gotten a lot of attention. MOFs have a structural variety and an unrivaled tenability, in addition to a wide range of potential uses, including medication delivery,[13] catalysis,[14] separations,[15] gas storage,[16] and sensing.[17] The need for adding appropriate recognition sites into MOFs to create a unique receptor has risen dramatically in tandem as a result of the advancement of MOF chemistry since it can improve the qualities of specialized applications. However, many chemical functions are incompatible conditions for MOF assembly.[18] Postsynthetic modification (PSM) is an easy and efficient approach for chemically tailing the inside of MOFs. Many materials with diverse physical and chemical characteristics may be created. PSM may introduce a variety of organic functional groups into MOF pores, including halides, alcohols, amines, imines, and azides.[19−23]

In this work, a novel ratiometric and spectrophotometric sensor for Hg^{2+}, Co^{2+}, and Al^{3+} ion detection based on a functionalized MOF named Al-MIL-53-N═SA-Br has been reported. The synthesis of Al-MIL-53-N═SA-Br was via a Schiff-base reaction in which a covalent attachment was found between the MOFs (Al-MIL-53-NH$_2$) and 5-bromo salicylaldehyde. The spectral properties of the robust Al-MIL-53-N═SA-Br sensor show it as a highly sensitive sensor for detecting the Hg^{2+}, Co^{2+}, and Al^{3+} ions. Under the optimum conditions, the selectivity of the developed Al-MIL-53-N═SA-Br sensor was examined in the company of several interfering ions. The stability of the Al-MIL-53-N═SA-Br sensor was also examined after storage for 3 months. To our knowledge, this is the first report showing a facile and highly efficient strategy to prepare smart and robust nanosensors, which can detect Hg^{2+}, Co^{2+}, and Al^{3+} ions in aqueous media. The Al-MIL-53-N═SA-Br sensor's field applicability was proven using a tap water sample from the research lab.

■ EXPERIMENTAL SECTION

Materials and Reagents. All the compounds utilized in this investigation are readily accessible in the market and were utilized without additional purification. In all our trials, we utilized ultrapure water and ethanol. AlCl$_3$·6H$_2$O (98%) and 2-aminaterephthalic acid (NH$_2$-H$_2$BDC) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Aqueous solutions of Co^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Na^+, K^+, Cd^{2+}, Hg^{2+}, and Fe^{3+} were prepared from their chloride salts. Fe^{2+} was prepared from ammonium ferrous sulfate and used immediately. All these salts were purchased from Sigma-Aldrich Co., (St Louis, USA).

Detection of the Hg^{2+}, Co^{2+}, and Al^{3+} Ions in an Aqueous Solution. The spectroscopic responses of Al-MIL-53-N═SA-Br to various metal cations in an aqueous solution were studied. At room temperature, M^{n+}@Al-MIL-53-N═SA-Br was prepared by introducing the (5 mg) Al-MIL-53-N═SA-Br powder into an aqueous solution (10 mL, 0.2 ppm) of M^{n+} (M^{n+} = Co^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Na^+, K^+, Cd^{2+}, Hg^{2+}, Fe^{2+}, and Fe^{3+}). After that, the mixes were 10 s of sonication to create the metal-ion-included suspension that was employed in the spectrophotometric measurements.

Recognition of the Ultratrace of Hg^{2+}, Co^{2+}, and Al^{3+} Ions. In a variety of pH solutions, the Al-MIL-53-N═SA-Br sensor was used to determine a definite concentration of Hg^{2+}, Co^{2+}, and Al^{3+} ions. About 5 mg of the Al-MIL-53-N═SA-Br sensor was added to a series of 10 mL solutions adjusted raising pH values (within 2−11 range) and containing 0.1 ppm of Hg^{2+}, Co^{2+}, and Al^{3+} ions. These solutions were then sonicated for 10 s. The suspension M^{n+}@Al-MIL-53-N═SA-Br was analyzed by UV−vis spectrometry after equilibration, in which the signal saturation of the Al-MIL-53-N═SA-Br nanosensor absorbance spectrum was reached.

Removal of Hg^{2+}, Co^{2+}, and Al^{3+} Ions from Aqueous Media. 50 mg of Al-MIL-53-N═SA-Br sensor was in the middle of two frits (1/16, 20 m, Análisis Vnicos, Tomelloso, Spain) into a 1 mL propylene cartridge that is empty (Análisis Vnicos) for the solid-phase extraction (SPE) cartridges. Then, 10 mL of 5.0 ppm of Hg^{2+}, Co^{2+}, and Al^{3+} ions solutions at pH 8.0, 8.0, and 7.0, respectively, at a flow rate of 0.1 mL min^{-1}, were put onto the SPE material. The Hg^{2+}, Co^{2+}, and Al^{3+} ions were measured before and after the elimination, a procedure using an ICP-atomic emission spectrometer (ICP-AES).

Determination of Hg^{2+}, Co^{2+}, and Al^{3+} Ions in Tap Water. The Al-MIL-53-N═SA-Br sensor's field applicability was proven using a tap water sample from the research lab. The water samples were spiked with various quantities of Hg^{2+}, Co^{2+}, and Al^{3+} ions, followed by a recovery experiment. Finally, spectrophotometric measurements were performed, and the findings were compared with the ICP-AES results.

■ RESULTS AND DISCUSSION

Characterization of the Prepared Al-MIL-53-N═SA-Br Sensor. The experimental PXRD pattern of the synthesized Al-MIL-53-NH$_2$ was quite like the one that had been prepared before.[21] The sharp peaks in Figure S1 demonstrate the

Scheme 1. Synthetic Route to the Condensation of the 5-Bromo Salicylaldehyde with Al-MIL-53-NH$_2$ and Formation of the Al-MIL-53-N═SA-Br Sensor
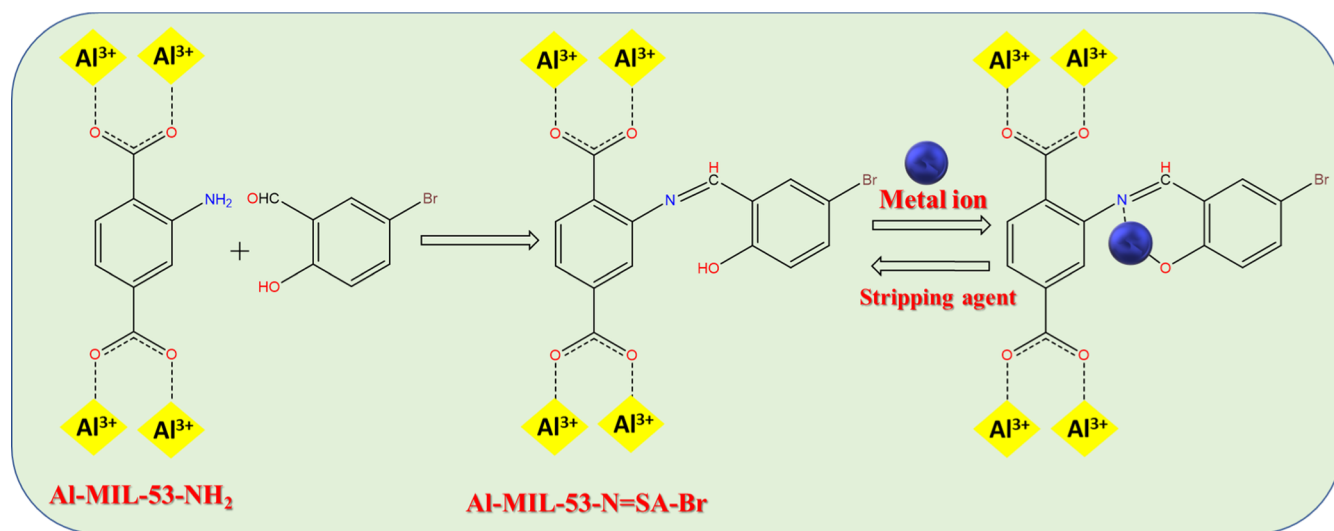
framework's excellent crystallinity and confirm the successful fabrication of Al-MIL-53-NH$_2$. Because the amine groups were not implicated in the construction of the framework in this study, they are capable of undergoing chemical changes. The product generated as Al-MIL-53-N═SA-Br was described using PXRD analysis after the amine groups interacted with 5-bromo salicylaldehyde (Scheme 1). There was no obvious loss of crystallinity following imine production, and the fundamental lattice structure of the MOF Al-MIL-53-NH$_2$ did not change after postsynthesis (Figure S1).[21−23] Furthermore, the hue shifted from light yellow of the MOF Al-MIL-53-NH$_2$ to pale red of the Al-MIL-53-N═SA-Br, indicating the successful imine formation. Fourier transform infrared (FTIR) spectroscopy was also used to demonstrate the production of C═N, as shown in Figure S2. In the framework of Al-MIL-53-NH$_2$, the two distinctive vibrational bands of the free −NH$_2$ group occur at 3496 and 3383 cm^{-1}. In the spectrum of the robust Al-MIL-53-N═SA-Br, the intensity of these two bands had significantly decreased, demonstrating that there was little unreacted −NH$_2$ within the pores of the Al-MIL-53-NH$_2$.[21−23] The bending vibrational mode of the NH$_2$ group is responsible for the a rather strong band that occurs at 1580 cm^{-1}. In the postsynthetic functionalized Al-MIL-53-N═SA-Br IR spectra, this sharp peak had also decreased, and a new band subsequent to the C═N group developed at 1434 cm^{-1}.[22,23] The band corresponding to 2-aminoterephthalic acid's C−N stretching vibrations shifted from 1010 to 1000 cm^{-1}, indicating the amino group's transition. As indicated in Scheme 1, the Al-MIL-53-N═SA-Br possesses two binding sites (N and O) that can be coordinated with metal ions.

The Al-MIL-53-NH$_2$ and Al-MIL-53-N═SA-Br nanoparticles are both made up of consistently formed nanoparticles with diameters between 50 and 100 nm, according to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) pictures (Figure 1). It shows that, following functionalization, Al-MIL-53-NH$_2$ was stable. We also found that, after reacting 5-bromo salicylaldehyde with Al-MIL-53-NH$_2$, particle size and shape remained nearly unchanged. Figure S3 shows the N$_2$ adsorption−desorption isotherms of Al-MIL-53-NH$_2$ and Al-MIL-53-N═SA-Br. After reacting 5-bromo salicylaldehyde with Al-MIL-53-NH$_2$, the
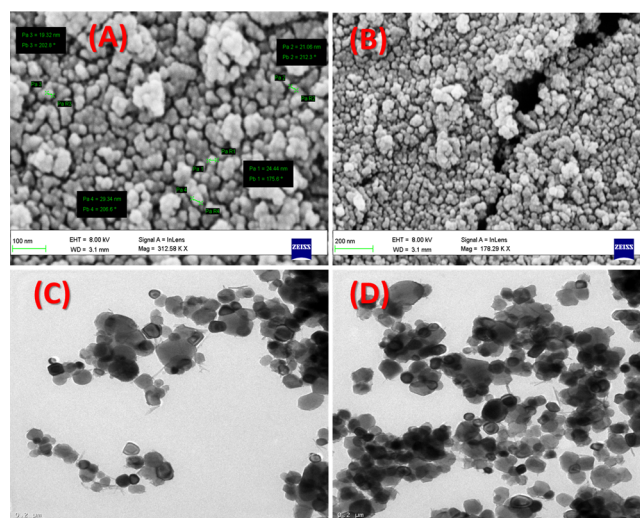

Figure 1. FESEM and TEM images of (A,C) the Al-MIL-53-NH$_2$ and (B,D) Al-MIL-53-N═SA-Br.

BET surface area of Al-MIL-53-NH$_2$ decreased from 667 to 584 m^2 g^{-1}. This shows that despite the 5-bromo salicylaldehyde interacting with the amino group, the Al-MIL-53-N═SA-Br still has well-structured channels and a large surface area.

Detection of the Hg^{2+}, Co^{2+}, and Al^{3+} Ions. The potential of Al-MIL-53-N═SA-Br for sensing the Hg^{2+}, Co^{2+}, and Al^{3+} ions in an aqueous solution was examined. The as-prepared Al-MIL-53-N═SA-Br (5 mg) samples were finely powdered and suspended in aqueous solutions containing various metal ions (Co^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Na$^+$, K$^+$, Cd^{2+}, Hg^{2+}, Fe^{2+}, and Fe^{3+}) (10 mL, 0.5 ppm). The solution was then ultrasonically mixed for 10 s to create the metal-ion-included MOF suspension. At room temperature, these metal ions were detected spectrophotometrically. The corresponding absorption spectra reveal that different metal ions have varied impacts on the Al-MIL-53-N═SA-Br absorption spectrum. When Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$, Cd^{2+}, Fe^{2+}, and Fe^{3+} react with Al-MIL-53-N═SA-Br, the absorption intensity at 394 nm stays essentially unaltered and only displays a little or
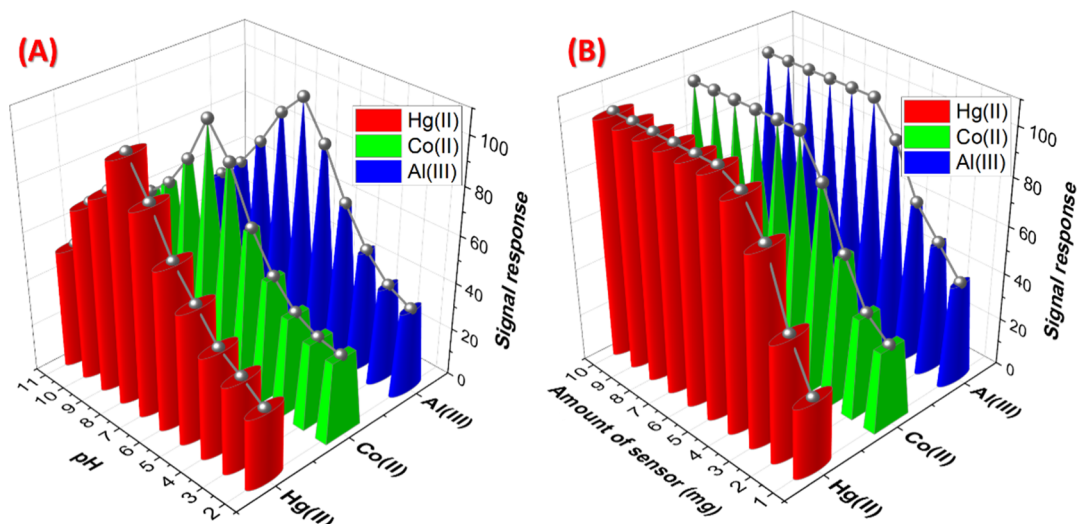
Figure 2. Effect of pH on the signal response for the detection of Hg^{2+}, Co^{2+}, and Al^{3+} ions (0.5 ppm) using 5 mg of the Al-MIL-53-N=SA-Br sensor at room temperature (A). Effect of the amount of the Al-MIL-53-N=SA-Br sensor on the signal response for the detection of Hg^{2+}, Co^{2+}, and Al^{3+} ions (0.5 ppm) at room temperature and pH 8.0, 8.0, and 7.0, respectively (B).
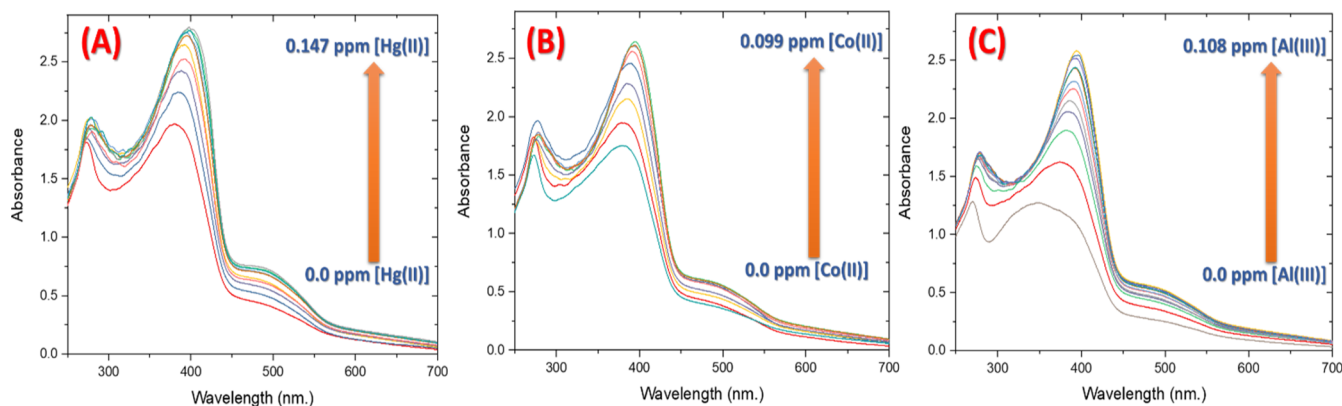

Figure 3. Absorption spectra of 5 mg of Al-MIL-53-N=SA-Br distributed in 10 mL aqueous solutions with various concentrations of Al-MIL-53-N=SA-Br (A) Hg^{2+} ions at pH 8, (B) Co^{2+} at pH 8, and (C) Al^{3+} at pH 7.

minor influence. After contact with the ions Hg^{2+}, Co^{2+}, and Al^{3+}, the absorption intensity of Al-MIL-53-N=SA-Br dramatically rises (Figure 3). This property might be beneficial for detecting Hg^{2+}, Co^{2+}, and Al^{3+} ions selectively using the absorption spectra increase when Hg^{2+}, Co^{2+}, and Al^{3+} ions are added to the Al-MIL-53-N=SA-Br sensor. The mechanism for the interaction of the sensor Al-MIL-53-N=SA-Br with the Hg^{2+}, Co^{2+}, and Al^{3+} ions was investigated. As shown in Scheme 1, the Hg^{2+}, Co^{2+}, and Al^{3+} ions can be coordinated with the nitrogen of the imine group and the oxygen of the phenolic group of the 5-bromo salicylaldehyde.

The effect of pH for detecting the Hg^{2+}, Co^{2+}, and Al^{3+} ions was tested by measuring the absorption spectra of 10 mL solutions containing 0.5 ppm of Hg^{2+}, Co^{2+}, or Al^{3+} at different pH values ranging from 2 to 11 using buffer solutions. Figure 2A indicates that the maximum intensities of the Al-MIL-53-N=SA-Br sensor were at pH of 8.0, 8.0, and 7.0 for detecting the Hg^{2+}, Co^{2+}, and Al^{3+} ions, respectively. To detect the appropriate amount of the Al-MIL-53-N=SA-Br sensor for detecting the Hg^{2+}, Co^{2+}, and Al^{3+} ions, a wide range (1−10 mg) of the sensor was used. The concentrations of the Hg^{2+}, Co^{2+}, and Al^{3+} ions were kept constant (0.5 ppm) at their optimal pHs. The results of the signal responses demonstrated

in Figure 2B showed that, with increasing the amount of the Al-MIL-53-N=SA-Br sensor, the absorption spectral intensity increases till it reaches a maximum value when using 5.0 mg of the Al-MIL-53-N=SA-Br sensor.

Analytical Parameters and the Calibration Graph. The robust Al-MIL-53-N=SA-Br sensor's physical features, such as its porosity, particle size morphology, and large surface area, are beneficial in allowing binding of the target ions in sensing assays and a high recognition capacity. The concentration-dependent absorption measurements were taken to better quantify the response of the Al-MIL-53-N=SA-Br sensor's absorption spectra to Hg^{2+}, Co^{2+}, and Al^{3+} ions. Therefore, in the detection of Hg^{2+}, Co^{2+}, and Al^{3+} ions, the intensities of the absorption bands can be used as a reference parameter. The specific detection range (DR) of the Hg^{2+}, Co^{2+}, and Al^{3+} ion-sensing device was determined by spectrophotometric research employing UV−vis spectroscopy. It was performed by watching the signaling change in the Al-MIL-53-N=SA-Br sensor's absorbance spectra after the Hg^{2+}, Co^{2+}, and Al^{3+} ions were added. As shown in Figure 3, the absorption intensities of the suspension Al-MIL-53-N=SA-Br sensor increase accordingly upon the increase in the Hg^{2+}, Co^{2+}, and Al^{3+} concentrations. These can enable the calibrating
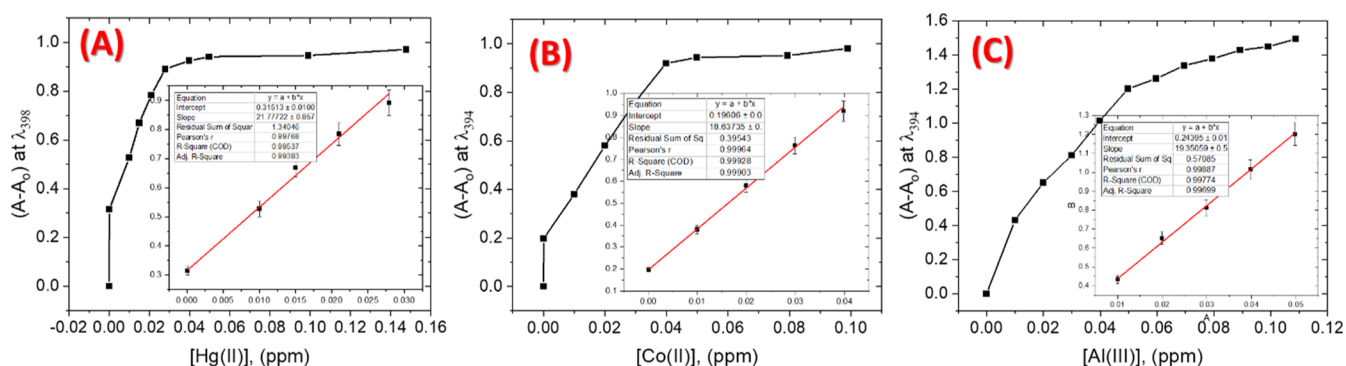
Figure 4. Absorption spectra of 5 mg of Al-MIL-53-N═SA-Br distributed in 10 mL aqueous solutions with various concentrations of (A) Hg^{2+} ions at pH 8, (B) Co^{2+} at pH 8, and (C) Al^{3+} at pH 7.

Table 1. Efficiency of the Suspension Al-MIL-53-N═SA-Br Sensor in Terms of Accessibility and Sensitivity during the Recognition of the Hg^{2+}, Co^{2+}, and Al^{3+} Ions[a]

metal ion	pH	R_t (S)	LOD (ppb) (M)	LOQ (ppb) (M)	D_R (ppb) (M)
Hg^{2+}	8	30	1.52	4.60	0.09−27.9
			7.56×10^{-9}	2.29×10^{-8}	4.98×10^{-10} to 1.49×10^{-7}
Co^{2+}	8	30	0.60	1.82	0.09−39.8
			1.02×10^{-8}	3.10×10^{-8}	1.69×10^{-9} to 6.78×10^{-7}
Al^{3+}	7	30	2.14	6.50	9.99−49.7
			7.95×10^{-8}	2.41×10^{-7}	3.71×10^{-7} to 1.85×10^{-6}

[a]Limit of detection (LOD), limit of quantitation (LOQ), detection range (D_R), and response-time (R_t) by the second (s).

Table 2. Spectrophotometric Results for Hg^{2+}, Co^{2+}, and Al^{3+} Ion Determination Using Various Previously Published Reagents/Sensors and Our Al-MIL-53-N═SA-Br Sensor

metal ion	reagent/sensor	D_R	LOD	refs
Hg^{2+}	iodide and rhodamine B	25−1350	10	25
	bis(4-(dimethylamino)phenyl)methanethione on MOF	0.5−150	0.8	26
	xylidyl blue	20−1000	4.65	27
	2-mercaptobenzothiazole	25−2500	7.0	28
	diphenylthiocarbazone	100−2500	20	29
	5-methylthiophene−2-carboxaldehyde ethylenediamine	830−8600	17.9	30
	Al-MIL-53-N═SA-Br	0.09−27.9	1.52	this work
Co^{2+}	bis(salicylaldehyde)orthophenylenediamine	100−15,000	15	31
	2-[2-cefpodoxime proxtel azo]2-paracetamole	1000−7000	500	32
	1-hexadecyl-3-methylimidazolium chloride	150−2000	70	33
	5-(4-hydroxy-3,5-dimethylbenzylidene)thiazolidine-2,4-dione	500−14,000	11	34
	1-[4-[(2-hydroxynaphthalen-1-yl)methylideneamino] phenyl]ethanone	0.45−10	0.08	35
	(Z)-2-((2-hydroxynaphthalen-1-yl)diazenyl)terephthalic acid on silica nanotubes	5−240	4.55	36
	Al-MIL-53-N═SA-Br	0.09−39.8	0.60	this work
Al^{3+}	8-hydroxyquinoline	0.1−20.0	0.032	37
	6-hydroxychromone-3-carbaldehyde-(3′-hydroxy-2′-naphthaleneformyl) hydrazone	270−1350	80	38
	aurintricarboxylic acid ammonium salt on mesoporous silica nanospheres	2.0−70	3.5	39
	quercetin on cetyltrimethylammonium bromide	20−500	7	40
	2,20,3,4-tetrahydroxy-30,50-disulphoazobenzene	50−1600	5	41
	alizarin red S	5.0−320	2	42
	Al-MIL-53-N═SA-Br	9.99−49.7	2.14	this work

measurement of Hg^{2+}, Co^{2+}, and Al^{3+} ions in the concentration range from 0.0 to 0.148 ppm (Figure 4). The chemical Al-MIL-53-N═SA-Br sensor provided a one-step and easy detecting approach for the measurement of Hg^{2+}, Co^{2+}, and Al^{3+} ions without the use of complicated instruments, according to the findings. With a correlation coefficient of R^2 = 0.998, the calibration curves roughly follow a linear connection between the absorption intensities and the Hg^{2+}, Co^{2+}, and Al^{3+} concentrations, as shown in Figure 4. The limit of detection (LOD) calculated from the standard deviation

(SD) of the blank and calibration sensitivity (slope of calibration line) LOD = 3.3 SD/sensitivity[24] was calculated for each metal ion, as shown in Table 1.

At low concentrations of Hg^{2+}, Co^{2+}, and Al^{3+} ions, the calibration plots of the Al-MIL-53-N═SA-Br sensor revealed a linear association (Figure 4, insets). These curves revealed that Hg^{2+}, Co^{2+}, and Al^{3+} ions have the highest sensitivity over a wide range of concentrations. The low LOD obtained (see Table 1) revealed that the generated Al-MIL-53-N═SA-Br sensor had a better identification of the target ions than
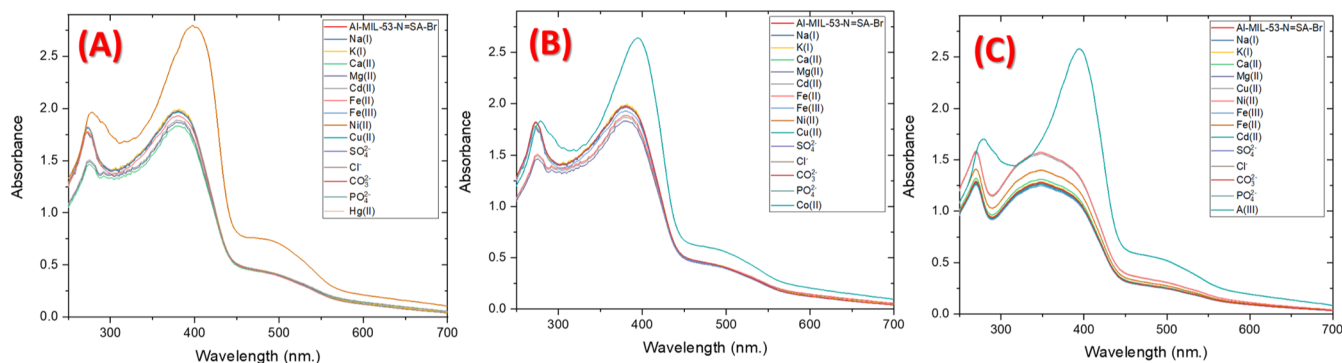
Figure 5. Under ideal conditions, the absorption spectra of the Al-MIL-53-N═SA-Br sensor (blank) following numerous foreign cations and anion additions (pH 8.0, 8.0, and 7.0; 5 mg of the Al-MIL-53-N═SA-Br sensor and 10 mL volume). The cations listed are 5.0 ppm of Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cd^{2+}, Fe^{2+}, and Fe^{3+}. The interfering anions are 5.0 ppm of Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}. (A) Hg^{2+} ions at pH 8, (B) Co^{2+} at pH 8, and (C) Al^{3+} at pH 7.

Table 3. Spectrophotometric Method Results in the Determination of the Hg^{2+}, Co^{2+}, and Al^{3+} in the Milli-Q Water and Tap Water Samples Using the Al-MIL-53-N═SA-Br Sensor

				Al-MIL-53-N═SA-Br senor			
samples	metal ion	added (ppb)	found[a] (ppb) ICP-AES	found[a] (ppb)	SD[a]	(RSD %)	recovery (%)
Milli-Q water	Hg^{2+}	15	14.90	15.02	0.058	0.38	100.8
		30	30.02	29.96	0.337	1.12	99.8
		50	50.02	49.98	0.048	0.09	99.9
	Co^{2+}	15	15.02	14.98	0.048	0.32	99.7
		30	30.10	29.81	0.414	1.38	99.0
		50	50.01	49.95	0.169	0.33	99.8
	Al^{3+}	15	15.01	14.99	0.185	1.23	99.8
		30	30.04	30.24	0.508	1.68	100.6
		50	50.00	49.95	0.110	0.22	99.9
tap water	Hg^{2+}	15	15.09	15.08	0.113	0.75	99.93
		30	29.19	30.02	0.185	0.62	102.8
		50	50.5	50.11	0.101	0.20	99.2
	Co^{2+}	15	15.10	15.25	0.155	1.02	100.9
		30	30.07	30.22	0.162	0.54	100.4
		50	50.19	50.14	0.056	0.11	99.9
	Al^{3+}	15	15.29	15.23	0.109	0.73	99.6
		30	30.30	30.31	0.153	0.51	100.0
		50	50.25	50.29	0.085	0.17	100.1

[a]Mean of five determinations at the 95% confidence level.

reagents/sensors produced using other methods.[25−42] Table 2 shows a comparison of our Al-MIL-53-N═SA-Br sensor's results with several previously described techniques for determining Hg^{2+}, Co^{2+}, and Al^{3+} ions using other reagents/ sensors. Our suggested Al-MIL-53-N═SA-Br sensor has a lower LOD than the other reagents/sensors, according to the data.

Selectivity. Selectivity, in addition to sensitivity, is a significant consideration for evaluating the performance of the proposed Al-MIL-53-N═SA-Br sensor. The selectivity of the developed Al-MIL-53-N═SA-Br sensor in the occurrence of numerous interfering ions was investigated in the optimal circumstances mentioned above. First, the interfering cations and anions were introduced to the robust Al-MIL-53-N═SA-Br sensor under ion-sensing conditions with known concentrations (5.0 ppm). The cations used for this study are Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cd^{2+}, Fe^{2+}, and Fe^{3+}. Also, the anions used are Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} (5.0 ppm). The absorption spectra of the Al-MIL-53-N═SA-Br sensor (blank) for Hg^{2+}, Co^{2+}, and Al^{3+} ions did not vary much at max,

according to our findings (Figure 5). The ion tolerance limit was set at the highest level, resulted in an absorbance measurement error of less than 5%. Except for Cu^{2+} and Ni^{2+}, which were well masked using 0.2 M $S_2O_3^{2-}$, the majority of the interfering ions did not create a significant interference. The Hg^{2+} ions were easily determined using the Al-MIL-53-N═SA-Br sensor in the presence of Al^{3+} ions by adding 0.1 M acetate as a masking agent. It was observed that there is no effect of anions on the Al-MIL-53-N═SA-Br sensor. The Al-MIL-53-N═SA-Br sensor was also unaffected by huge concentrations of alkaline metal or alkaline-earth metal ions. This demonstrates that other metal ions' interference may be ignored.

Ion-Reversible Sensing System. Hg^{2+} was effectively removed from the utilized sensor after a simple treatment with 0.2 M thiourea as a stripping agent. The Co^{2+} and Al^{3+} ions were also removed from the Al-MIL-53-N═SA-Br sensor using 0.2 M ethylenediaminetetraacetic acid (EDTA). To release the Hg^{2+}, Co^{2+}, and Al^{3+} ions and get a "metal-free" probe surface, we repeated these procedures numerous times

using a liquid exchange technique. After various regeneration/reuse cycles (i.e., 6), the Al-MIL-53-N═SA-Br sensor showed just a little influence on sensitivity. The robust covalent link between the 5-bromo salicylaldehyde and the amino of the Al-MIL-53-NH2 structure accounts for the sensor's excellent efficiency after a six times reversibility.

Stability of the Al-MIL-53-N═SA-Br Sensor. The optical sensor is technically advantageous due to the extended shelf-life of the Al-MIL-53-N═SA-Br sensor efficiency. The robust Al-MIL-53-N═SA-Br sensor was tested for long-term storage for at least 3 months. Controlling the potential leaching of the chromophore during storage was achieved by a direct condensation of 5-bromo salicylaldehyde with Al-MIL-53-NH2, direct adsorption, or without the application of any surface modification. The absorption spectra of the Al-MIL-53-N═SA-Br sensor did not change after 3 months of storage in a dark container, according to our findings. The Al-MIL-53-N═SA-Br solid sensor has significantly superior stability than sensors based on the physisorbed probe molecules.[43−53] The Al-MIL-53-N═SA-Br sensor, which uses a direct condensation of 5-bromo salicylaldehyde with Al-MIL-53-NH$_2$, offers a simple sensing design concerning sensitivity, selectivity, repeatability, and shelf-life.

Adsorption Capacity. The amount of sorbent required for the quantitative holding of the analyte from a solution is determined by the sorption capacity. Under the conditions described above, this material was utilized as an SPE sorbent to test the Al-MIL-53-N═SA-Br sensor's adsorption capability. The resulting capacity of the sorbent was 88.3, 100.8, and 104.4 mg of Hg^{2+}, Co^{2+}, and Al^{3+} ions per gram of the Al-MIL-53-N═SA-Br sensor, respectively. As a result, the robust Al-MIL-53-N═SA-Br sensor may also be utilized as a basic preconcentrator.

Application. The developed Al-MIL-53-N═SA-Br probe was tested on a tap water sample acquired from our lab to assess the field applicability of our detection technology. The tap water sample was further polluted with standard solutions of these ions since the contamination by Hg^{2+}, Co^{2+}, and Al^{3+} ions in the tap water sample were lower than the designed sensor's LOD. This approach was repeated five times and yielded the same result, indicating that our sensor has a good accuracy and performance. The sensitivity of this solid Al-MIL-53-N═SA-Br sensor was compared to results gained by the ICP-AES. The results of both Milli-Q water and tap water analyzed by our robust Al-MIL-53-N═SA-Br nanosensor are found to be in excellent agreement with those gotten by ICP-AES with a confidence level of 95% and a relative SD (RSD %) that has not increased more than 1.68%, as shown in Table 3. Therefore, this confirms the utility of the developed Al-MIL-53-N═SA-Br nanosensor for the detection of the Hg^{2+}, Co^{2+}, and Al^{3+} ions in real water samples. Table 3 shows also that the recoveries of the Hg^{2+}, Co^{2+}, and Al^{3+} ions were between 99.0 and 102.8%. Although the genuine samples are complicated and contain components that might cause calculations to fail, the spiked Hg^{2+}, Co^{2+}, and Al^{3+} ions can be retrieved with great precision from these samples. This suggests that the suggested approach may be utilized to determine Hg^{2+}, Co^{2+}, and Al^{3+} ions in actual samples with a good selectivity and sensitivity.

CONCLUSIONS

A solvothermal process was used to make a strong MOF (Al-MIL-53-NH$_2$). The amine group of the Al-MIL-53-NH$_2$ was transformed into an imine group via a Schiff-base reaction with 5-bromo salicylaldehyde. FTIR spectroscopy was used to assess if the imine group formed successfully. The fundamental lattice structure of Al-MIL-53-NH$_2$ was not affected during the imine production stage, according to the results. The absorption properties of the as-prepared functionalized Al-MIL-53-N═SA-Br were also investigated. The results show that the Al-MIL-53-N═SA-Br can be used as an ultrasensitive sensor for Hg^{2+}, Co^{2+}, and Al^{3+} ions. The mechanism of the sensor's interaction with the analyte was studied. The absorption spectral intensity of Al-MIL-53-N═SA-Br linearly increased upon increasing the concentration of Hg^{2+}, Co^{2+}, and Al^{3+} ions in a wide range of concentrations, with a detection limit of 1.52 ppm of Hg^{2+} ion (7.56×10^{-9}). Thus, it is believed that the robust Al-MIL-53-N═SA-Br probe is an outstanding candidate for the detection of the Hg^{2+}, Co^{2+}, and Al^{3+} ions, with a high sensitivity and an insignificant effect of competitive ions. According to ICH criteria, the recommended techniques were validated in terms of LOD, LOQ, linearity, and accuracy. Simple treatment using thiourea or EDTA can remove out the Hg^{2+}, Co^{2+}, and Al^{3+} ions from the used Al-MIL-53-N═SA-Br sensor and use it many times with a high efficiency. In addition, the Al-MIL-53-N═SA-Br sensor has a high adsorption capacity for these metal ions. This is the first research to our knowledge that shows a simple and efficient technique for making a smart and robust nanosensor that can detect Hg^{2+}, Co^{2+}, and Al^{3+} ions in aqueous media. In actual samples, the suggested approach may be utilized to determine Hg^{2+}, Co^{2+}, and Al^{3+} ions with a good selectivity and sensitivity.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02021.

> Detailed procedure for the synthesis of 5-bromo salicylaldehyde, preparation of Al-MIL-53-NH$_2$, preparation of Al-MIL-53-N═SA-Br, X-ray diffraction pattern of Al-MIL-53-NH$_2$ and Al-MIL-53-N═SA-Br, FTIR image of the Al-MIL-53-NH$_2$ and Al-MIL-53-N═SA-Br, and nitrogen adsorption−desorption isotherm of Al-MIL-53-NH$_2$ and Al-MIL-53-N═SA-Br (PDF)

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Notes

The authors declare no competing financial interest.

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