Metal-Organic Frameworks-Based Sensors for Detection of Toxic Environmental Contaminants

SARAH CLOUSE, MD ABU SHOHAG
and MD HUMAYUN KABIR

ABSTRACT

Continuous industrialization has led to the release of many heavy-metal pollutants from industrial wastes into the natural environment. In the recent decade, there is an increasing demand for accurate environmental pollution monitoring and control requires new sensing techniques with high sensitivity, selectivity, and reliability. Metal−organic frameworks (MOFs) have received considerable attention for environmental contaminant detection including anions, heavy metal ions, volatile organic compounds, and toxic gases because of their high surface area, porosity, large pore volumes, tunable structures, and open metal sites. A Fe^{3+} ion-selective electrochemical sensor was fabricated by depositing the synthesized Cu(TBC)-MOF on a glassy carbon electrode (GCE) and the electrochemical method was investigated in detail in an aqueous medium. The proposed Fe^{3+} ion sensor exhibited a linear relationship for current vs. Fe^{3+} ion concentration in the concentration range of 0.001 μM to 100 μM. The limit of detection value was found to be 0.52 μM in aqueous media which is lower than the acceptable value of iron in drinking water (0.3 mg/L). The presence of other ions such as Na^{+}, K^{+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Cl^{-}, NO_3^{-}, and SO_4^{2-} did not interfere with the detection of Fe^{3+} ions.

INTRODUCTION

The development of highly sensitive and selective sensors has been attracting great interest in detecting metal ions for improving and protecting our living environments and health. Iron Fe^{2+} plays a vital role in many biological processes [1-3]. It plays a crucial role in oxygen transport, cellular metabolism, and energy generation and serves as an essential component in myoglobin, hemoglobin, and cytochromes [4]. Living cells should maintain the optimum concentration of iron ions as its imbalance can cause severe diseases such as the imbalance in the concentration of iron may lead to severe

Sarah Clouse[1], Md Abu Shohag[2], and Md Humayun Kabir[1,*]
[1]Department of Chemistry and Physics, University of North Alabama, Florence, AL 35632
[2]Department of Engineering and Industrial Professions, University of North Alabama, Florence, AL 35632
*Corresponding Author's Email: hkabir@una.edu

diseases like Alzheimer's disease, Parkinson's disease, heart diseases, liver and kidney damage, and diabetes [5, 6]. In addition to the physiological role, the imbalanced concentration of Fe^{3+} ions in soil and water adversely affects the environment [7, 8]. Therefore, the development of chemosensors, which can be used to evaluate iron levels in environmental systems, is of great significance.

Various analytical techniques, such as fluorescence spectrometry, atomic absorption spectrometry (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), ion-pair chromatography, and voltammetry have been developed to detect metal ions in biological and environmental samples [9-11]. However, these techniques are expensive, laborious, and time-consuming, thereby making them less desirable for direct assays. In the recent decade, a large number of fluorometric- and colorimetric-based sensors have been developed for the detection of various analytes including Fe^{3+} and Fe^{2+} ions. Some investigators developed inorganic nanoparticle-based sensors, such as quantum dots (QDs) for the detection of Fe^{3+} [12]. However, some of the properties of these nanomaterials such as short-wavelength emission, low quantum yield, and poor selectivity have limited their applications in Fe^{3+} detection. To overcome this drawback, sensors based on electrochemical methods have become popular. Accordingly, many studies have explored the detection of numerous toxic heavy metal ions using nanocomposites on glassy carbon electrodes (GCEs) [13, 14].

Recently, metal–organic frameworks (MOFs) have attracted much attention for their unique physicochemical properties such as large surface areas, tunable structures, and optical properties [15]. Metal–organic frameworks (MOFs), also called porous coordination polymers, are a class of crystalline materials composed of metal ions or clusters interconnected by organic ligands. Their crystalline, porous structure and isoreticular synthesis make them excellent candidates for a wide range of applications including gas storage and separation, catalysis, and chemical sensing [16]. Recently a wide range of luminescent MOFs chemosensors for selective detection of heavy metal ions including Fe^{3+} have been reported [17, 18].

In this meeting, we aim to report the synthesis and characterization of copper(II)-benzene-1,3,5-tricarboxylate, $[Cu_3(BTC)_2]_n$-MOFs as an efficient electrochemical sensor for Fe^{3+} ion detection. The sensing of metal ions by $[Cu_3(BTC)_2]_n$-MOFs occurs by interaction of the metal ions with the open metal sites or ligand backbone such as uncoordinated carboxylate oxygen atoms, -COO- moieties. The easy fabrication, fast responses, and low detection limit make this approach very promising for Fe^{3+} detection.

MATERIALS AND METHODS

Reagents, Materials, and Equipment

Copper acetate, benzene-1, 3, 5 tricarboxylic acid (BTC), *N*, *N*′-dimethyl formamide (DMF), and Nafion were purchased from Sigma-Aldrich, USA, and used without further purification. Aqueous solutions were prepared by dissolving the appropriate salts in deionized water (18.2 MΩ·cm). Glassy carbon electrode (GCE) tips with an electrode diameter of 3.00 mm were sourced from CH Instruments Inc. A Keithley Source meter (model 2401) was used for sensor analysis during electrochemical sensor development.

[$Cu_3(BTC)_2$] Synthesis

Cu-BTC MOF was synthesized according to a previously reported procedure [19]. First, $Cu(NO_3)_2$ (0.876 g) and BTC (0.472 g) dissolved in a solvent mixture of 4 mL of *N*, *N*′-dimethylformamide (DMF), 4 mL of ethanol, and 4 mL of deionized water, then sealed with parafilm and further agitated for approximately 15 minutes. The mixture was then transferred and heated in an oven at 85°C for ~20 hours. The MOF crystals were then transferred to a centrifuge tube and washed with DMF. The yielded product was then dried under vacuum at 200 °C.

Working/Sensing Electrode Fabrication

During the sensing electrode fabrication process, the synthesized $Cu_3(BTC)_2$ was mixed with ethanol to form a slurry. This $Cu_3(BTC)_2$ slurry was then deposited on the flat surface of the GCE as a thin uniform layer and dried under ambient conditions. Next, a drop of Nafion solution was added to the dry modified GCE, which was then dried at room temperature. Conductive binding agent Nafion was used to obtain the optimum binding strength of $Cu_3(BTC)_2$ on the GCE. Nafion was conductive and improved the electron transfer rate and the conductance of the fabricated electrochemical sensor. The desired electrochemical analysis was then performed, predominantly using a Keithley Electrometer, with the modified GCE with the structure $Cu_3(BTC)_2$/Nafion binder/GCE and a Pt-wire used as the working and counter electrodes, respectively. $FeCl_3$ was diluted with deionized water to form various solutions with concentrations in the range of 0.001 μM to 100 μM, which were tested as analytes.

RESULTS AND DISCUSSION

The [$Cu_3(BTC)_2$] was synthesized using $Cu(NO_3)_2$ and benzene-1, 3, 5 tricarboxylic acid in DMF/ethanol by hydrothermal method [19]. Figure 1 shows the formation of $Cu_3(BTC)_2$ MOF by hydrothermal method. The $Cu_3(BTC)_2$ MOF formation revealed that twelve carboxylate oxygen atoms of two ligands 1,3,5-benzene tricarboxylate bind to the 4-coordination site for each of the three Cu^{2+} ions of the formula unit.

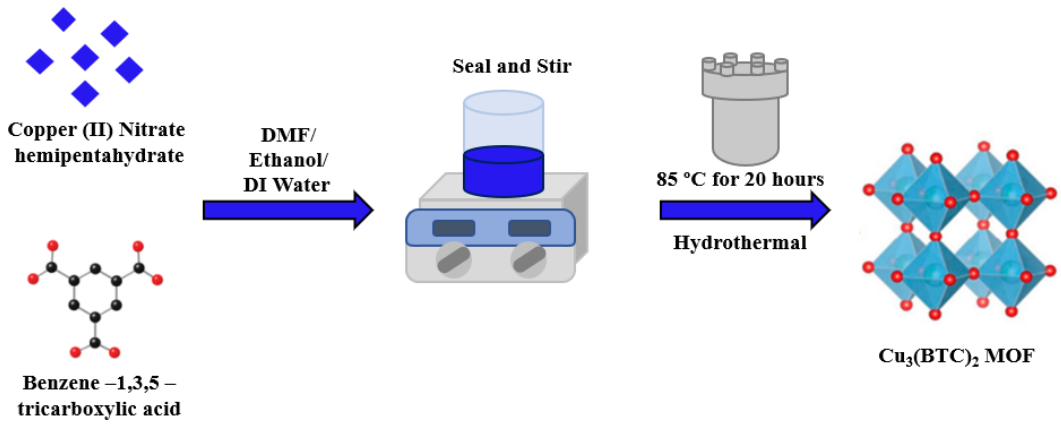

Figure 1. Synthesis of $Cu_3(BTC)_2$ by hydrothermal method.

Each metal completes its pseudo-octahedral coordination sphere with an axial H_2O ligand opposite to the Cu-Cu geometry. The interconnection of Cu-paddle wheel unit with the tridentate 1,3,5-benzene tricarboxylate linker bond is repeated so that infinitely cubic frameworks are formed [20].

Powder X-ray Diffraction (XRD) Analysis

The [$Cu_3(BTC)_2$] product was characterized by powder X-ray diffraction (XRD) in order to ensure a high purity of the crystalline phases. The XRD patterns of the $Cu_3(BTC)_2$ and $Cu_3(BTC)_2$/GO composite are presented in Figure 2. The XRD patterns are identical to those reported by other investigators [19]. The final results obtained greenish-blue powder which is dried at 100 ^oC. The sharper peaks in the range area of 2θ from 20° to 30° assumed to represent the peak of the coordinated and or uncoordinated solvent (Figure 2). Additionally, the synthesized $Cu_3(BTC)_2$ exhibit peaks corresponding to CuO at 2θ = 35.4° and 38.5°.

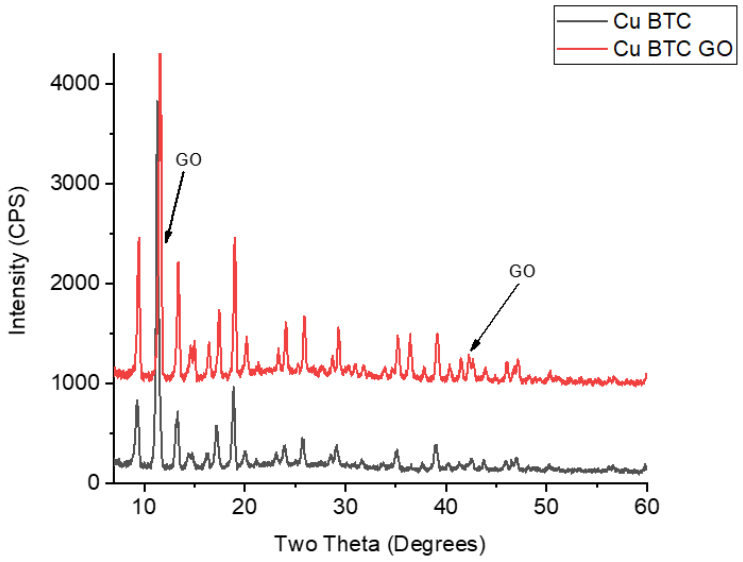

Figure 2. Powder XRD patterns of $Cu_3(BTC)_2$ and $Cu_3(BTC)_2$/GO composite MOFs.

FTIR Analysis

The FTIR spectra of $Cu_3(BTC)_2$ and BTC are shown in Figure 3. $Cu_3(BTC)_2$ shows a broad absorption band at 3400 cm^{-1} which is attributed to coordinated water in the MOF framework. The Absorption peak at 1720 cm^{-1} corresponds to the stretching vibration of C=O shown in BTC which after forming $Cu_3(BTC)_2$ shifted to 1631 cm^{-1}, indicating the deprotonation process occurred in C=O bond. This shift proved that the carboxylate ion participated in the MOF framework formation. Moreover, the peak at 727 cm^{-1} may be attributed to Cu-O stretching vibration in which the oxygen atom coordinated with Cu^{2+} indicates that the Cu-based MOF is successfully synthesized [21].

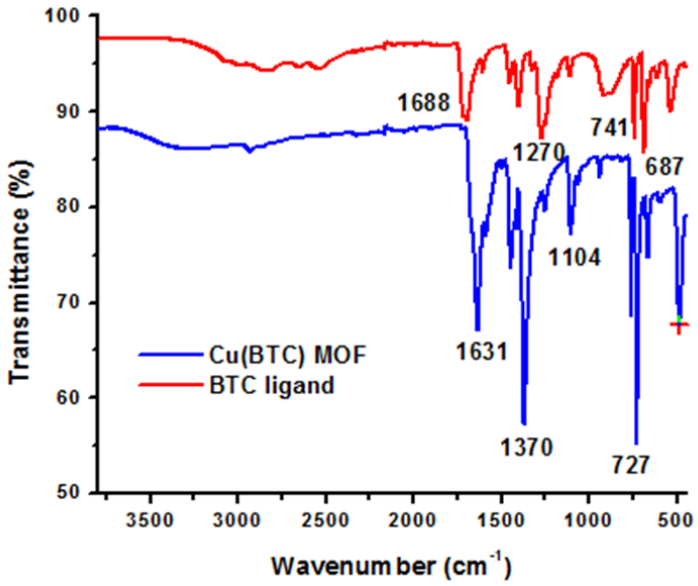

Figure 3. FTIR spectra of $Cu_3(BTC)_2$ and BTC.

Metal Ions Detection: I-V Measurement

The detection of metal ions was performed in an aqueous solution at room temperature. First, standard stock solutions of Fe^{3+}, Zn^{2+}, Co^{2+}, Pb^{2+}, and Cd^{2+} with different concentrations were prepared by dissolving metal salts in deionized water. The working electrode of the sensor was prepared by the deposition of a drop of $Cu_3(BTC)_2$ PC onto a GCE. Afterward, a drop of 5% Nafion solution was applied as a binder. Figure 4 shows the fabrication of the working electrode of the sensor.

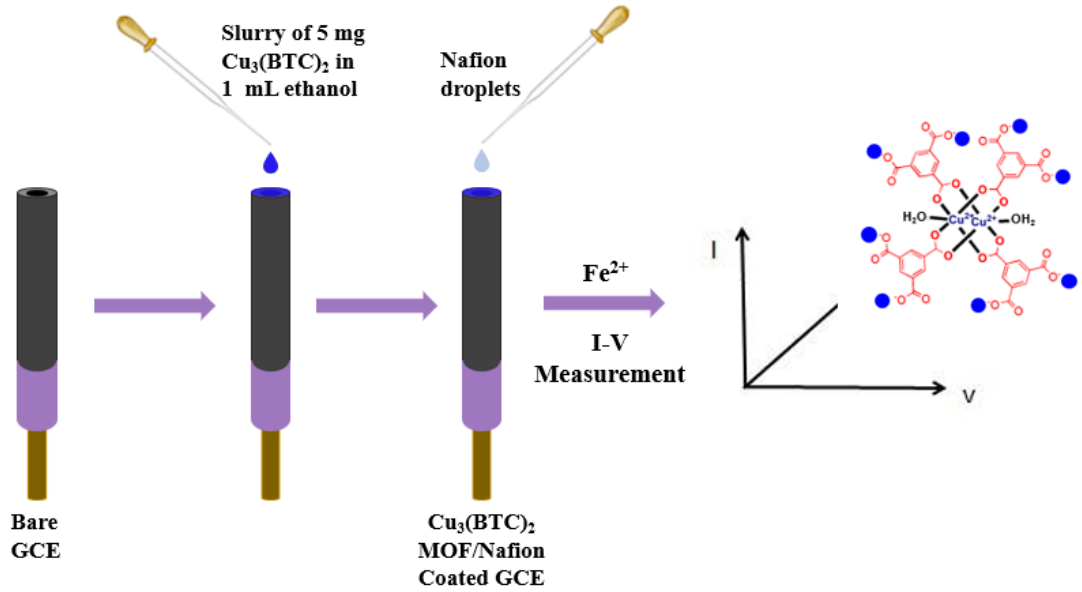

Figure 4. Schematic representation of the fabrication of $Cu_3(BTC)_2$/Nafion/GCE electrochemical sensor for Fe^{2+} detection.

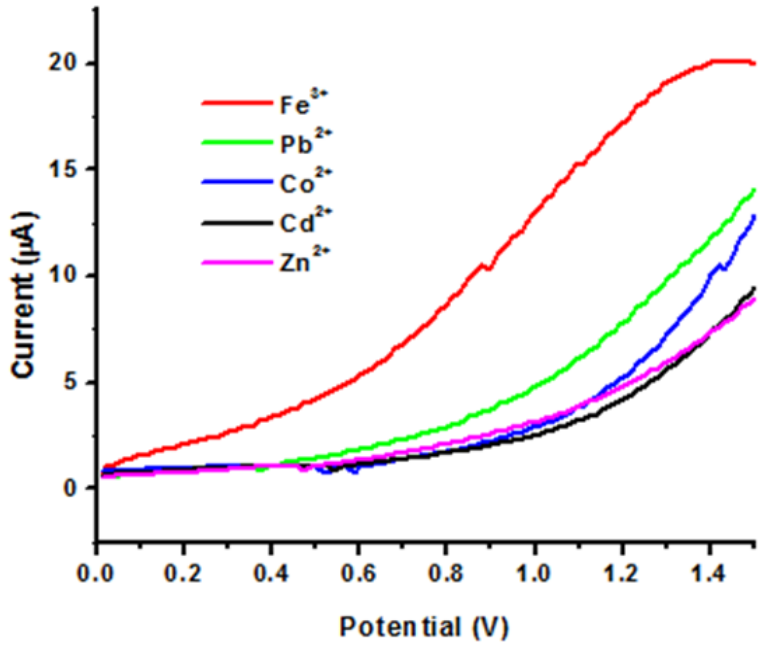

Figure 5. Analysis of the selectivity of the fabricated sensor for analytes with identical concentrations (1 mM) in 1M KNO_3 electrolyte.

At the start of the electrochemical analysis, a number of toxic heavy metal ions were investigated, and the electrochemical responses were measured. The observed current resulting from the applied potential was measured at the surface of the $Cu_3(BTC)_2$ /Nafion/GCE working electrode. Figure 5 shows the resulting electrochemical responses toward various metal ions such as Na^+, K^+, Mg^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, Co^{2+}, and Zn^{2+} with identical concentrations (1 mM). Among them, Fe^{3+} ions showed the highest current response among other cations. Considering this high current response, Fe^{3+} ions were selectively detected as toxic metal ions using $Cu_3(BTC)_2$/Nafion/GCE sensor. This selectivity study revealed that the fabricated sensor showed the highest current for Fe^{3+} ions compared with other cations. Furthermore, this sensor was applied to analyze concentration variations Fe^{3+} ions. As shown in Figure 6, the electrochemical responses to Fe^{3+} ions were well-defined and could be distinguished in the concentration range of 0.1 μM to 0.1 mM. The I–V responses to Fe^{3+} ions varied with the Fe^{3+} ion concentration. Therefore, the electrochemical responses were concluded to be directly proportional to the Fe^{3+} ion concentration.

Selectivity

Selectivity is one of the most important factors when detecting metal ions in real complex samples. To determine the electrochemical activity of other metal ions toward the Cu(BTC)/Nafion/GCE sensor probe, various metal ions (Na^+, K^+, Mg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, and Zn^{2+}) were analyzed at concentrations of 0.1 mM at applied potentials of 0 to +1.5 V, and compared with Fe^{3+} ions under identical conditions. Interference effects were tested for Na^+, K^+, Cd^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+} coexisting with Fe^{3+}. This clearly showed that the original electrochemical response toward Fe^{3+} ions was not changed in the presence of other metal ions.

Sensing Mechanism

A mechanism for Fe^{3+} ion detection was proposed for Cu(BTC)/Nafion/GCE in KNO_3 electrolyte, as shown in Figure 5. The Fe^{3+} ion is absorbed on the surface of the Cu(BTC)-coated GCE. The oxygen atoms in Cu(BTC) interact with the Fe^{3+} ions through chelation. This interaction enhances the current in the electrochemical method. At a low Fe^{3+} ion concentration, there is less surface coverage of Fe^{3+} ions on Cu(BTC)/Nafion/GCE film, which causes the surface reaction to proceed steadily. By increasing the Fe^{3+} ion concentration, the surface reaction is increased significantly due to the surface area (Cu(BTC)/Nafion/GCE assembly) contacted with Fe^{3+} ions. Further increasing the Fe^{3+} ion concentration on the Cu(BTC)/Nafion/GCE surface resulted in a more rapid increase in the current response due to the larger area covered with Fe^{3+} ions. Figure 6 shows the electrochemical response to Fe^{3+} ions in the concentration range of 0.001 μM to 100 μM.

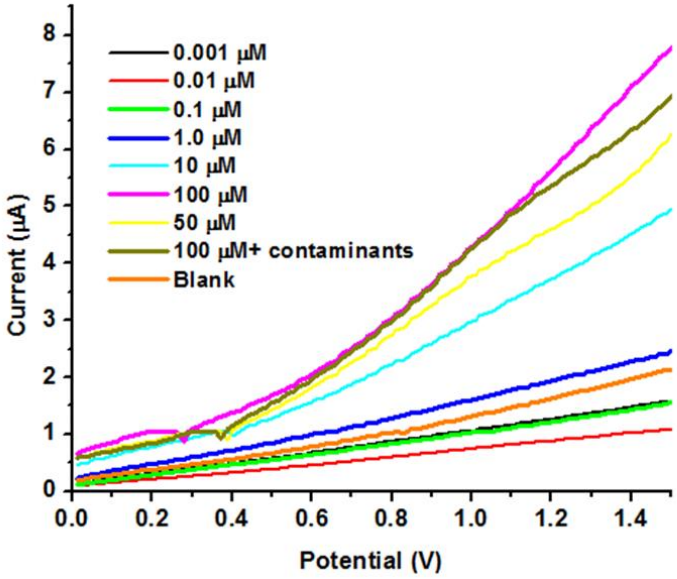

Figure 6. I–V responses to Fe^{3+} ions at concentrations from 0.001 μM to 100 μM (in 1M KNO_3) for the $Cu_3(BTC)_2$/Nafion/GCE electrochemical sensor.

CONCLUSION

In this study, the Fe^{3+} ion sensor probe was fabricated by coating a GCE with DMF solution of Cu(BTC). This fabricated Cu(BTC)/Nafion/GCE electrode was applied to detect Fe^{3+} ions using an electrochemical approach. The proposed Fe^{3+} cationic sensor was satisfactory in terms of sensitivity, reproducibility, detection limit, response time, and stability.

REFERENCES

[1] J. Yin, Y. Hu, J. Yoon, Fluorescent probes and bioimaging: alkali metals, alkaline earth metals and pH, Chemical Society Reviews, 44 (2015) 4619-4644.

[2] X. Zhou, S. Lee, Z. Xu, J. Yoon, Recent Progress on the Development of Chemosensors for Gases, Chemical Reviews, 115 (2015) 7944-8000.
[3] T. Hirayama, K. Okuda, H. Nagasawa, A highly selective turn-on fluorescent probe for iron(ii) to visualize labile iron in living cells, Chemical Science, 4 (2013) 1250-1256.
[4] X. Liu, N. Li, M.-M. Xu, J. Wang, C. Jiang, G. Song, Y. Wang, Specific colorimetric detection of Fe3+ ions in aqueous solution by squaraine-based chemosensor, RSC Advances, 8 (2018) 34860-34866.
[5] N. Abbaspour, R. Hurrell, R. Kelishadi, Review on iron and its importance for human health, Journal of research in medical sciences : the official journal of Isfahan University of Medical Sciences, 19 (2014) 164-174.
[6] S. Altamura, M.U. Muckenthaler, Iron Toxicity in Diseases of Aging: Alzheimer's Disease, Parkinson's Disease and Atherosclerosis, Journal of Alzheimer's Disease, 16 (2009) 879-895.
[7] M. Rehman, L. Liu, Q. Wang, M.H. Saleem, S. Bashir, S. Ullah, D. Peng, Copper environmental toxicology, recent advances, and future outlook: a review, Environmental Science and Pollution Research, 26 (2019) 18003-18016.
[8] G.R. Rout, S. Sahoo, Role of iron in plant growth and metabolism, Reviews in Agricultural Science, 3 (2015) 1-24.
[9] S. Ghaseminezhad, D. Afzali, M.A. Taher, Flame atomic absorption spectrometry for the determination of trace amount of rhodium after separation and preconcentration onto modified multiwalled carbon nanotubes as a new solid sorbent, Talanta, 80 (2009) 168-172.
[10] J.L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, A comparison between ICP-MS and AFS detection for arsenic speciation in environmental samples, Talanta, 51 (2000) 257-268.
[11] Y. Lu, X. Liang, C. Niyungeko, J. Zhou, J. Xu, G. Tian, A review of the identification and detection of heavy metal ions in the environment by voltammetry, Talanta, 178 (2018) 324-338.
[12] J. Shangguan, J. Huang, D. He, X. He, K. Wang, R. Ye, X. Yang, T. Qing, J. Tang, Highly Fe3+-Selective Fluorescent Nanoprobe Based on Ultrabright N/P Codoped Carbon Dots and Its Application in Biological Samples, Analytical Chemistry, 89 (2017) 7477-7484.
[13] R.M. El-Shishtawy, H.A. Al-Ghamdi, M.M. Alam, Z.M. Al-amshany, A.M. Asiri, M.M. Rahman, Development of Cd2+ sensor based on BZNA/Nafion/Glassy carbon electrode by electrochemical approach, Chemical Engineering Journal, 352 (2018) 225-231.
[14] F.M. Aqlan, M.M. Alam, A.M. Asiri, M.E.M. Zayed, D.A. Al-Eryani, F.A.M. Al-Zahrani, R.M. El-Shishtawy, J. Uddin, M.M. Rahman, Fabrication of selective and sensitive Pb2+ detection by 2,2′-(−(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))diphenol by electrochemical approach for environmental remediation, Journal of Molecular Liquids, 281 (2019) 401-406.
[15] R. Fu, S. Hu, X. Wu, Rapid and sensitive detection of nitroaromatic explosives by using new 3D lanthanide phosphonates, Journal of Materials Chemistry A, 5 (2017) 1952-1956.
[16] Z. Zhang, Z.-Z. Yao, S. Xiang, B. Chen, Perspective of microporous metal–organic frameworks for CO2 capture and separation, Energy & Environmental Science, 7 (2014) 2868-2899.
[17] C.-H. Chen, X.-S. Wang, L. Li, Y.-B. Huang, R. Cao, Highly selective sensing of Fe3+ by an anionic metal–organic framework containing uncoordinated nitrogen and carboxylate oxygen sites, Dalton Transactions, 47 (2018) 3452-3458.
[18] L. Li, S. Shen, W. Ai, S. Song, Y. Bai, H. Liu, Facilely synthesized Eu3+ post-functionalized UiO-66-type metal-organic framework for rapid and highly selective detection of Fe3+ in aqueous solution, Sensors and Actuators B: Chemical, 267 (2018) 542-548.
[19] S. Najafi Nobar, Cu-BTC synthesis, characterization and preparation for adsorption studies, Materials Chemistry and Physics, 213 (2018) 343-351.
[20] S.S.Y. Chui, S.M.F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, A Chemically Functionalizable Nanoporous Material [Cu3(TMA)2(H2O)3]n, Science, 283 (1999) 1148-1150.
[21] W.W. Lestari, M. Adreane, C. Purnawan, H. Fansuri, N. Widiastuti, S.B. Rahardjo, Solvothermal and electrochemical synthetic method of HKUST-1 and its methane storage capacity, IOP Conference Series: Materials Science and Engineering, 107 (2016) 012030.