Application of Different Analysis Methods Based on Metal-Organic Frameworks for Different Heavy Metal Ions Detection

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Abstract: The heavy metal pollution is a huge problem to the world as it is extremely harmful to human health and ecological balance. There are various kinds of heavy metal, like copper, lead and mercury which is widely distributed on the earth. However, traditional analysis methods to detect heavy metal ions are quite time-consuming and expensive. In order to achieve a higher level of detection, a new determining strategy is in urgent need. Metal-organic frameworks (MOFs) is a relatively advanced group of materials for many purposes including chemical sensing. As it has many comparative advantages, for example, high electrocatalytic activity and large surface area, it shows great potential in this area. When MOFs-based functional materials are combined with other distinct techniques, the "chemical nose" can even get more sensitive. For a specific kind of heavy metal ions, a unique detection method should be prepared to detect them with high sensitivity and selectivity. This research will introduce some advanced and up-dated heavy metal determining strategies based on MOFs materials. The synthesis of some MOFs-based materials is also included in this research in detail. It is quite meaningful to discover a new material and explore its potential application. As the technology is developing so rapidly, MOFs materials will definitely dominate in the future.

1 INTRODUCTION

The word "heavy metal" means those elements containing an atomic density above 5 g/cm^3, which must show metallic properties (Kim, 2019). Typically, they occur in rater low concentration, but they can be found all through the crust of the earth. In common, heavy metal ions include transition metals, post-transition metals, and lanthanides. Some metals are essential to the entire human metabolism and they possess the functions indispensable for various biological process, like copper, zinc, or selenium. However, due to anthropogenic activities, heavy metal pollution has also become a global issue and is widely discussed. Since industrial revolution, the increasing demand for exploration of the natural resources on the earth has exceeded people's expectations. In light of this, after heavy metals enter the environment, it will cause serious environmental pollution and destroy the natural ecosystem due to the high toxicity of heavy metals and their migration and transformation properties. The heavy metal pollution can also be increased by some natural causes including volcanic activities and soil erosion (Mishra G. K, 2017).

Heavy metal plays an important role in human body and environment. Some of the heavy metals serve as microelements which can support metabolism, speed up the enzyme production and enhance the enzyme activity. However, the presence of these heavy metal ions in an exceeding amount is highly likely to cause irreversible problems to both human health and the environmental protection. As the development of industrialization is getting faster, people should pay attention to these potential hazards. For example, the overuse of pesticides containing mercury in agriculture will cause mercury pollution. The mercury is one of the most hazardous and poisonous heavy metal because it will do harm to the nerves and the brain. The damage to the nervous system results in mental diseases like depression which is a huge threat to human health. Also, the mercury pollution is also destructive to the environmental protection and ecological balance. Due to the existence of biological magnification, it will cause series of problems to the whole food chain such as some fatal diseases. In addition, the reproductive system may be destroyed since there will be a significant decline in the quantity of reproduction. In light of this, if human release too

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much mercury to the environment, people will suffer from both health and environmental hazard. Besides mercury, lead and chromium are other examples of harmful heavy metals. When lead and lead containing compounds enter the human body, it will immediately do harm to various systems like digestive system, endocrine system, nervous system and cardiovascular system. Chromium and its containing compounds are already classified as cancerogens which may cause cancer. In addition, since chromium ions are deadly to most aquatic organisms, too much chromium will significantly do harm to ecological balance as a result. Therefore, it is quite meaningful and important for human to pay attention to these threats. The toxicological homes of metalloids are continuously delivered about by means of way of their fashion to structure covalent bonds, most important them to bind covalently with herbal groups. In addition, given that metals can't be damaged down and are non-biodegradable, when the heavy metals are absorbed by means of capacity of human bodies, they bio-accumulate in our system. This is categorized as unsafe due to the fact the bio-accumulation reasons natural and physiological complications. For some heavy metals, they are essential to useful resource existence and are commonly required for some physiological functions. Nevertheless, these heavy metals can moreover be toxic if they current in massive amounts. Thus, the detection of heavy steel ions is pretty massive to human health and the environmental protection (Ding, 2021).

A traditional way to detect heavy metal ions is the atomic absorption spectrometry. The principle is that all atoms can absorb light with specific wavelengths. However, this kind of technique hold the disadvantage of high instrument complexity and instrument cost. Another way to detect heavy metal ions is to use electrochemical aptasensor-based technology. Nevertheless, the reproducibility and balance of electrochemical sensors want greater improvement. For different detection methods, enzyme evaluation for example, even though it has excessive sensitivity, it is challenging to discover a single heavy metallic ion and it is solely successful for water samples. For immunoassay, it is genuine that the detection can be extraordinarily quickly and it can acquire an excessive selectivity, however the practice of metallic ion monoclonal antibodies is very tough and polyclonal antibodies are challenging to meet the precise necessities for steel ions. Thus, a miniaturized heavy metal ion detector with excellent sensitivity, selectivity and stability is demanded. In fact, luminescent MOF based detectors show great potential in the field of heavy metal protection (Chen, 2021). This material can be combined with other analytical methods for better application. As a result, this research mainly introduces different sensing methods based on MOFs materials and used to detect heavy metal ions, including mercury ions (Hg^{2+}), lead ions (Pb^{2+}) and cadmium ions (Cr^{3+}).

The aim of this article is to explore the potential of various techniques based on MOFs materials for detection of different heavy metal ions. The MOFs materials have lots of advantages in this field such as higher selectivity and greater sensitivity. In modern society, the demand for hazards detectors with such quality is getting increasingly urgent. For instance, it is necessary for households to pay attention to the potential risk of mercury poisoning. Also, for environmental protection sectors, they have suffered from various pollutions like heavy metal pollution for a long time. However, all current detectors have some limitations like high maintaining cost. Therefore, with the help of MOFs materials, all of these concerns will be eliminated. It is extremely certain that the detectors based on MOFs will dominate the field of heavy metal ions detection and other sensing fields.

2 DETECTION OF HG^{2+}

The detection of Hg^{2+} is quite significant because it is highly likely to cause digestive and neurological diseases for human due to its toxicity, non-degradability and water stability. In addition, because Hg^{2+} is the most stable form that mercury can exist, it will cause serious consequences like environmental pollution even at low concentrations. However, although traditional detection methods may be efficient in Hg^{2+} detection, they are extremely expensive and they take large amount of time, like gas chromatography and anodic stripping voltammetry. Therefore, developing new methods are in urgent need for detection of Hg^{2+}.

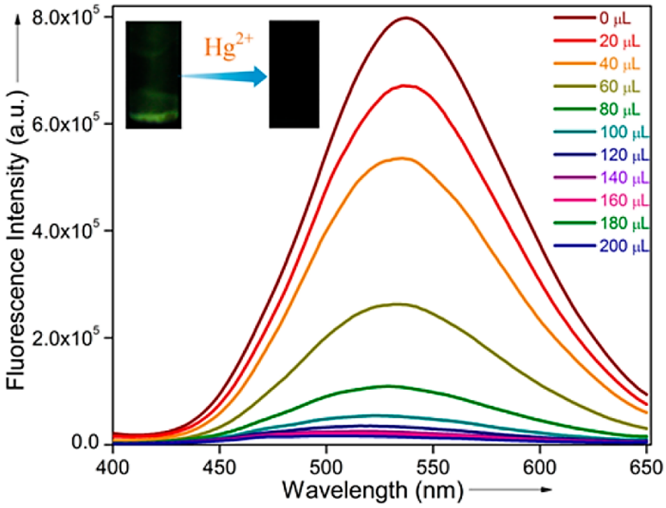

Figure 1: Change of the fluorescence intensity of the used MOFs materials in the presence of different concentrations of Hg^{2+} (Samanta, 2018).

MOFs-based functional materials have been widely used to construct different sensing methods and have recently been used to achieve the goal. Most MOFs-based Hg^{2+} sensors are based on chemosensors and they can be identified in to two sets. The first group of MOFs-based sensors have nitrogen or amine groups at center, which are able to coordinate to Hg^{2+}. Another group of sensors have sulfur-rich probes, which allows Hg^{2+} to bind with the sulfur center. Nevertheless, such probes have some limitations. First of all, amines and sulfides will inevitably be oxidized by the air during long-period storage. Therefore, the results of detection will be negatively affected. In addition, the sulfur-based probes cannot offer a proper signal in an environment that is full of sulfur if there's too much mercury presented. In order to solve these problems, scientists have carried out a lot of progress. Instead of the use of any amine or sulfur to function, chemodosimeter-based method is employed. With the assist of chemodosimeter, the purpose analyte can react with dosimeter molecules to furnish everlasting signals. It is well-known that the Hg^{2+} ions react with alkyne organizations by way of ability of viable of oxymercuration response in the presence of water. Therefore, the new sensing method based on MOFs can be fabricated to detect the presence of Hg^{2+} in water sources.

Since in large amount of cases, the sensing and determining of the focused analytes has been obtained, the water balance is the most good-sized standards for sensible functions. A crew of MOFs named UiO sequence MOFs possess excessive chemical steadiness supported by way of its secondary constructing unit. For example, Samanta et al. prepared a new functionalized MOF (UiO-66@Butyne) and then deigned a new sensing method to detect Hg^{2+} in water (Samanta, 2018). Water-stable zirconium-based MOFs have been synthesized bearing butyne agencies as vigorous websites to cease up conscious of mercury ion. As UiO-66 is extraordinarily chemically stable, the butyne-functionalized UiO-66@Butyne is a practicable Hg^{2+} sensor due to the fact it can use an irreversible oxymercuration response to produce signal. With the assist of butyne functionality, the sensor can obtain excessive selectivity and sensitivity. As shown in Fig. 1, based on the different fluorescence intensity changes caused by different mercury ion concentrations, the detection limit of the constructed sensing method can reach 10.9 nM, showing the outstanding sensitivity. Although a sensor with mechanism based on reactions has failed to be mentioned up to now in the MOF database, this MOF-based sensor indicates tremendous doable in this field. Razavi et al. used the tetrazine-modified MOF to develop a dual solvent detection method for detection of mercury ion (Razavi, 2017). The prepared MOFs material has good luminescence properties and high stability. When it was used to construct a mercury ion detection method, the method showed great advantages, such as fast response time, high sensitivity, and good selection. In this work, the response time and sensitivity can reach 15 s and 1.8×10^{-6} M, respectively. And the developed sensing method based on MOFs shows a high selectivity, as shown in Fig. 2.

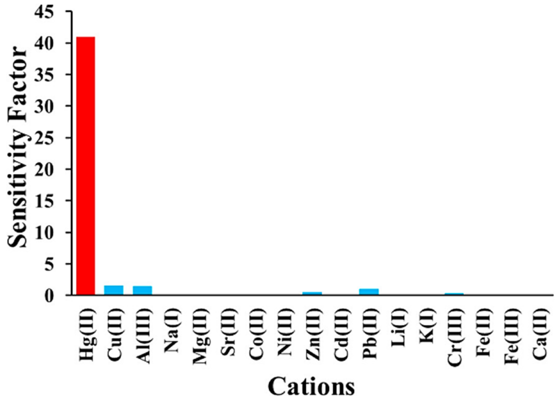

Figure 2: The selective analysis of the developed sensing method (Razavi, 2017).

3 DETECTION OF PB^{2+}

Heavy metallic ions are extremely harmful and dangerous pollutants since they will do harm to humans as well as atmosphere as a whole. Among all the harmful heavy metal ions, Pb^{2+} ions have been paid lots of attention because it can be released from various sources, such as smoking and industries. As lead accumulate over time, it will substitute some elements and tissues heading in the bone, leading to diseases like cancer and causing damage. In some extreme cases, the high amount consumption of lead may even result in death. As a result, in order to preserve human health and ecological sustainability, the detection of lead ions is necessary. Different types of lead ion detection methods have been developed, such as electrochemical sensing methods, colorimetric sensing methods, fluorescence sensing methods, etc. However, these methods more or less have their own drawbacks. The introduction of new functional materials and the development of new lead ion detection methods have received more and more attention. Scientists have done some researches to explore potential materials that are suitable for the determination of heavy metal ions, such as noble metal nanomaterials and graphene materials. However, the challenge is that the sensitivity and selectivity can't achieve a high level. Among these various materials, MOFs shows great adaptability because MOFs materials have high crystallinity and considerable porosity. As a result, a new detection method based on MOFs materials has been developed and used to realize the detection of lead ions.

Wang et al. used the prepared MOFs to develop a new electrochemical detection method for lead ions detection (Wang, 2013). The prepared MOFs material (MOF-5) was modified on the carbon paste electrode, which can be then used to adsorb lead ions in the solution, resulting in the change of the induction signal. The electrodes constructed with this material exhibited good electrochemical response behaviour and improved detection limit up to 4.9×10^{-9} M. in addition, as shown in Fig. 3, when using the prepared MOFs material to modify the functional electrode, the electrode can be used continuously for at least 50 times, showing excellent stability. Ding et al. used the MOFs material (UIO-66) to design an electrochemical sensing method for simultaneous detection of cadmium ions and lead ions (Ding, Wei, 2021). The synthesized MOFs material (UIO-66) was carbonized and then used to modify the electrode, thereby constructing a highly sensitive electrochemical detection method. The results show that the limit of detection for the developed electrochemical sensing method is 1.16 μg/L and 1.14 μg/L for cadmium ions and lead ions, respectively.

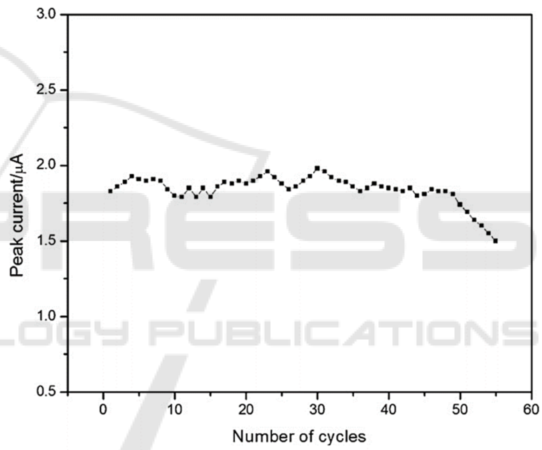

Figure 3: Cycle times of electrodes modified with the prepared MOFs materials (Wang, 2013).

4 DETECTION OF CR^{3+}

The detection of Cr^{2+} is quite significant because it is highly likely to cause digestive and neurological diseases. In addition, chromium(III) can bind with deoxyribonucleic acid in body, major to mutations or malignant cells and chromium(VI) is successful to cause genetic mutations in body. Therefore, once chromium ions exist in the air in large quantities, they are classified as serious air pollution with the resource of the American environmental security agency. Therefore, selective and touchy detection of chromium ion is quite significant. Also, it is in actuality really helpful for every human health and environmental protection. However, the ordinary detection strategies are commonly elaborate and high-priced for the dedication of Cr^{3+}. Nowadays, using the detection methods for the detection of Cr^{3+} with high selectivity has attracted a lot attention. In moderate of this, fluorescence-based MOFs for sensing Cr^{3+} are increased effective and perfect in distinction with these ordinary methods (Lv, 2016). Because they are accessible to use and they are no longer that expensive, they are higher cost-effective.

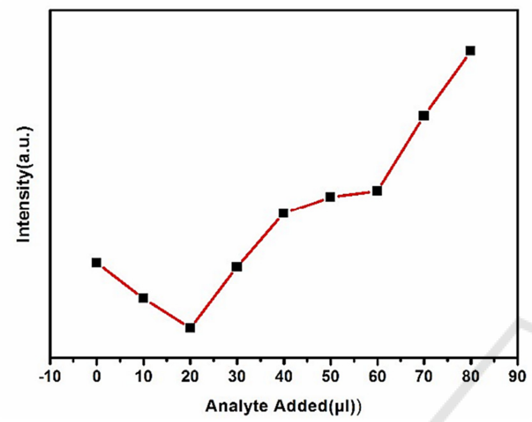

Figure 4: Change of the fluorescence intensity of NH_2-Zn-MOF in the presence of different concentrations of target metal ions (Lv, 2016).

$Zn(NO_3)_2 \cdot 6H_2O$, TPOM, NH_2-BDC, dimethyl-formamide and H_2O have been sealed into a stainless steel vessel. Then, the combination will be heated. Colourless rhombus crystals then would be acquired by way of filtration and washed. The suspension will be used for luminescent measurements. Since MOF have d10 metallic ions and fragrant natural ligands, they possess luminescent characteristics. In mild of this, DMF can be an applicable dispersion medium. The luminescent spectra of NH_2-Zn-MOF separated in DMF have been confirmed in room temperature. The results show that NH_2-Zn-MOF separated in MOF suggests a launch at 420 nm. The robust fluorescence emission of this type of MOF fabric is critical for its utility in heavy metallic detection. The fluorescence intensity of the NH_2-Zn-MOF can be changed by adding of the different concentrations of the target metal ions (see Fig. 4).

To find out the possible capability of the selectivity of the detection by using NH_2-Zn-MOF for chromium ions combined with different specific heavy metal ions such as iron ion. They choose Fe^{3+} as opposition ions which have the absolute fine quenching efficiency. By way of potential of examining the fluorescence spectra, scientists

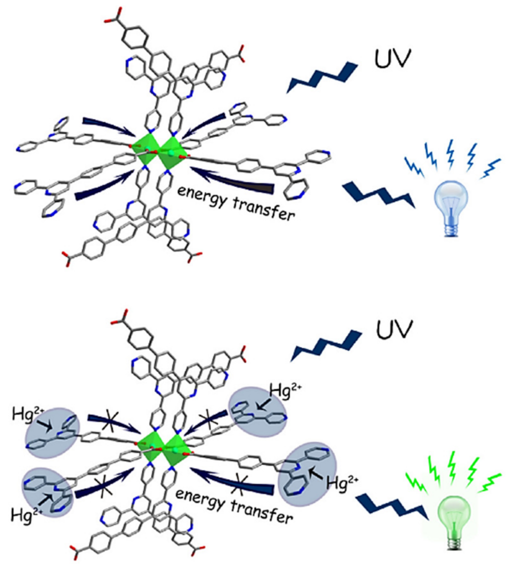

Figure 5: Schematic diagram of the mechanism of fluorescence detection of heavy metals based on MOFs materials (Xiao, 2018).

conclude that the fluorescence depth is lowering when they added iron ion into the solution. However, the widespread trend of luminescence intensity shows continuously greater desirable due to the addition of chromium ions. The effects factor out that the greater stage of selectivity is completed thru this type of MOF. The developed amino-decorated MOF which refers to NH_2-Zn-MOF indicates immoderate sensitivity towards chromium ions. As shown in Fig. 5, it is precisely because of the high sensitivity exhibited by different detection methods constructed based on MOFs-based functional materials, where MOFs materials have been widely used (Xiao, 2018).

5 CONCLUSION

As the heavy metal pollution is getting worse nowadays, it is necessary for scientists to explore a new detection strategy. The detection with high selectivity and sensitivity of chromium ion, mercury ion and lead ion can be achieved by MOFs-based functional materials. Chemodosimeter-based approach shows great potential in the field of mercury ion detection. MOF-5 is used to determine the presence of lead ion. For the detection of chromium ion, NH_2-Zn-MOF based technique shows greater advantage compared with other traditional methods because of its luminescent properties. Although the MOFs-based functional material is not that widely used in the contraction with other materials, it will definitely get increasingly popular and advanced with further research and exploration. With the help of MOFs-based functional materials to construct heavy metal detectors with high selectivity and sensitivity, people can get huge benefit from it in the field of health and environmental protection.

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