Removal of Hg^{2+} heavy metal ion using a highly stable metal-organic framework

Hossein Shayegan, Seyedeh Pegah Aledavoud, Zahra Seyfi Hasankola and Vahid Safarifard*

Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran.
Email: vsafarifard@iust.ac.ir; Fax: +98 21 73021415; Tel: +98 21 73228327

Abstract:

The zirconium-based metal-organic framework known as PCN-221 was successfully synthesized by the solvothermal method. Characterization of the MOF was performed using various techniques, such as FT-IR, XRD, UV-Vis, and SEM analysis. The MOF has then applied to rapidly and efficiently adsorption of mercury (Hg^{2+}) ions using an ultrasonic bath. Different parameters such as initial metal ion concentration, contact time, solution pH and adsorbent dose were investigated. The presence of a nitrogen-functionalized group in the porphyrin ligand in PCN-221 structure contributed to the absorption of mercury ions. The adsorption capacity of 233 mg g^{-1} was obtained for this adsorbent in less than 30 minutes at pH = 7. The experimental adsorption data for the PCN-221 MOF are well suited with the pseudo-second-order kinetic model (R^2 = 0.99), and adsorption isotherms of Pb^{2+} metal ions are in good agreement with the Langmuir model.

Keywords: Metal-organic frameworks; Hg^{2+}; Heavy metal ions; Removal; Adsorption

Introduction

As industry and agriculture grow rapidly, different contamination agents release in the environment leading to introducing into the food chain. Among the water pollution sources, heavy metals are considered as the most hazardous contaminants because of their low biodegradability and high toxicity to human health [1]. The term “heavy metal” is used for any metallic element with high density (more than 5 g/cm^3) (e.g. cadmium, mercury, arsenic, chromium, copper and, lead) [2]. Mercury (Hg) pollution enters into environments through industry products/by-products and processes [3], including the mining industry, batteries, pharmaceuticals, metallurgy, and badly damage the brain, kidneys, digestive system and nerves as well as causing birth defects [1]. Based on the United States Environmental Protection Agency (EPA) mandate, the concentration of mercury in water must not overpass 2 ppb in drinking water [3].

Common remediation techniques such as precipitation, ion exchange, reverse osmosis, bioremediation, electrolysis, and adsorption by various materials (activated carbon, chitosan, etc.) and so on were reported for removing heavy metals from wastewater [4]. Since traditional adsorbents suffer from lacking suitable capacity or high efficiency, novel promising adsorbents should be exploited [5].

Over the past decade, metal-organic frameworks (MOFs), composed from metal ions or clusters as metallic nodes and organic ligands through coordination bonds, have been in center of attention due to their unique porous structure with significant characteristics like high surface area, tunable chemical composition as well as various pore size distribution [6-8]. This subdivision of porous coordination polymers could exhibit a wide range of applications containing catalysis, drug delivery systems, molecular recognition, light-harvesting, selective sorption in liquid and gas phases, gas storage and separations [9-13]. On the basis of the selection of modified ligands or by MOF post functionalization, various functional groups can enhance the efficiency of MOFs due to providing more active sites to interact with target analytes [6, 8]. Based on the promising features of MOFs, they could act as a favorable candidate for heavy metal removal applications

EXPERIMENTAL SECTION

Materials and Measurements. Analytical grade chemicals for the preparation of PCN-221 were bought from Merck, Sigma-Aldrich, and others and utilized without further purification. 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP) were used to the preparation of PCN-221. *N*,*N*-dimethylformamide (DMF) was utilized as the solve.

Aqueous solutions of Ni^{2+}, Cr^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, As^{3+}, Fe^{3+} and, Al^{3+} were built from, $NiCl_2·6H_2O$, $Cr(NO_3)_2·9H_2O$, $Co(NO_3)_2·6H_2O$, $HgCl_2·2H_2O$, $Pb(NO_3)_2$, $Mn(OAc)_2·4H_2O$, $CdCl_2·2.5H_2O$, $NaAsO_2$, $FeCl_3·6H_2O$, and $Al(NO_3)_3·9H_2O$, respectively.

Synthesis of porphyrin (H_2TCPP)

The preparation of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP) linker was performed according to the Adler method [14]. Pyrrole (2.33 mmol) and 4-carboxybenzaldehyde (2.33 mmol) were dissolved in 100 mL propionic acid. The mixture was refluxed for 4h, and cooled to room temperature. After the mixture was brought down to room temperature, 100 ml of pure methanol was added and cooled with an ice bath stirrer. The deep-purple crystals are filtered and washed with methanol and hot water.

Synthesis of PCN-221

Briefly, PCN-221 was synthesized by the solvothermal reaction process, where H_2TCPP (50 mg), $ZrCl_4$ (35 mg) and acetic acid (0.4 ml) were dissolved in 10 ml of N,N′-dimethylformamide (DMF) in a Teflon reactor, and heated to 120 °C for 16 h. After cooling to room temperature, dark red crystals were obtained which were washed with DMF solvent.

RESULTS AND DISCUSSION

A comparison between as-synthesized and simulated PXRD patterns of PCN-221 shows that the structure of PCN-221 have been successfully synthesized (Fig.1a) [15, 16]. Moreover, comparison between the FT-IR spectra of pure porphyrin and Zr-MOF porphyrin is shown in Fig. 1b.

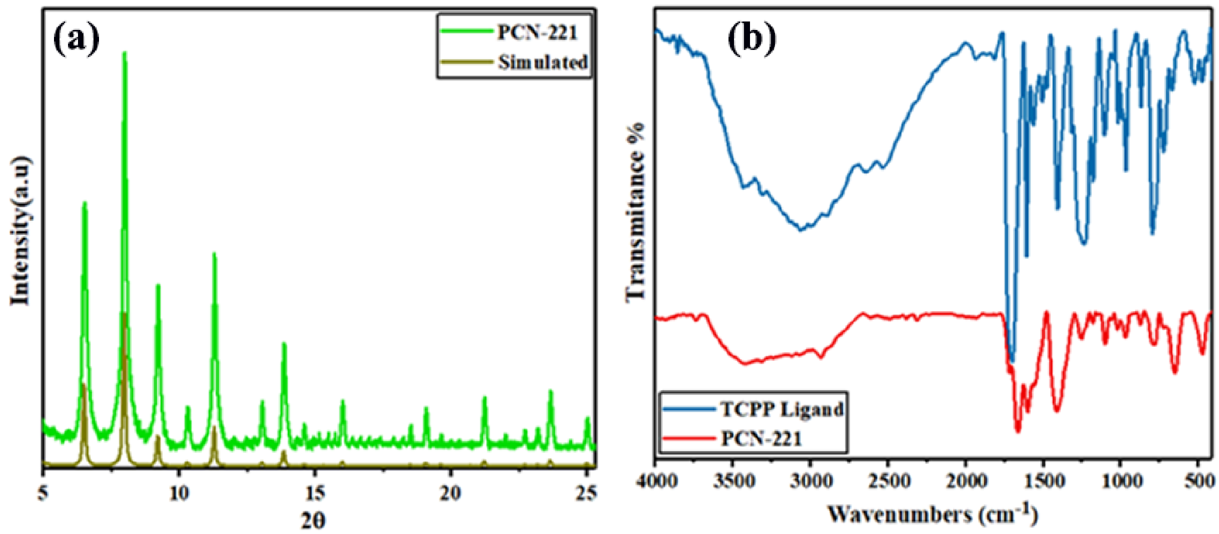

Figure 1. (a) PXRD of as-synthesized (green) and simulated (brown) PCN-221. (b) FT-IR spectra of TCPP Ligand (blue) and solvothermal synthesized of PCN-221 (red).

Heavy Metal Removal by PCN-221.

Heavy metal ions adsorption experiments were performed by adding 10 mg of the adsorbent to 50 ml of an aqueous solution containing mercury ions. $HgCl_2{\cdot}2H_2O$ was applied as the source of Hg(II). The pH of the solution was adjusted by adding 0.01 M HCl and 0.01 M NaOH, and experiments were performed at room temperature using an ultrasonic bath. The adsorbent was then separated by a centrifuge for 6 minutes in aqueous solution and the residual metal ions were measured.

Hg^{2+}Adsorption Studies for [PCN-221].

In order to evaluate the adsorbent performance, various parameters such as time of adsorbent contact with mercury ions in solution, and an initial amount of mercury ions, solution pH and adsorbent dose were evaluated by ultrasonic method at room temperature. In addition, the performance of adsorbent PCN-221 compared to other porous adsorbents was investigated, showing that the adsorbent exhibits acceptable adsorption capacity among the introduced adsorbents for adsorption of mercury ions.

Effect of pH.

The absorption process strongly depends on the pH range. First, 50 ppm of mercury solution was prepared to investigate the absorption performance of PCN-221. 0.01 g of absorbent was added to

50 ml of mercury-containing solution in separate containers. Fig. 3a and b show the effect of soluble pH on the absorption of mercury ions.

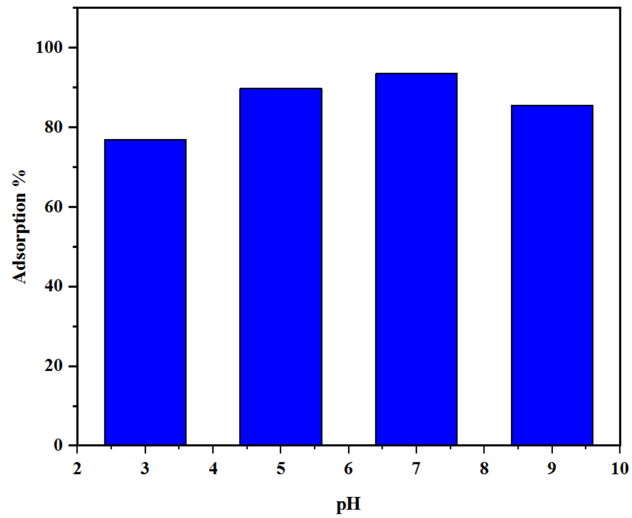

Figure 2. pH solution effect on Hg^{2+} ions adsorption efficiency for PCN-221.

Study of Sorption Kinetics.

Ultrasonic adsorption of mercury metal ions was performed by adsorbent PCN-221 to investigate the adsorption kinetics. Adsorption kinetics evaluates the method of chemical or physical adsorption of ions and includes pseudo-first-order, pseudo-second-order models and intra-particle diffusion. The correlation coefficient R^2 is the criterion for determining the adsorption kinetics. As can be seen in Fig. 3a and b, the correlation coefficient for the pseudo-second-order model (R^2=0.99) was higher than that for the pseudo-first-order model for mercury ions.

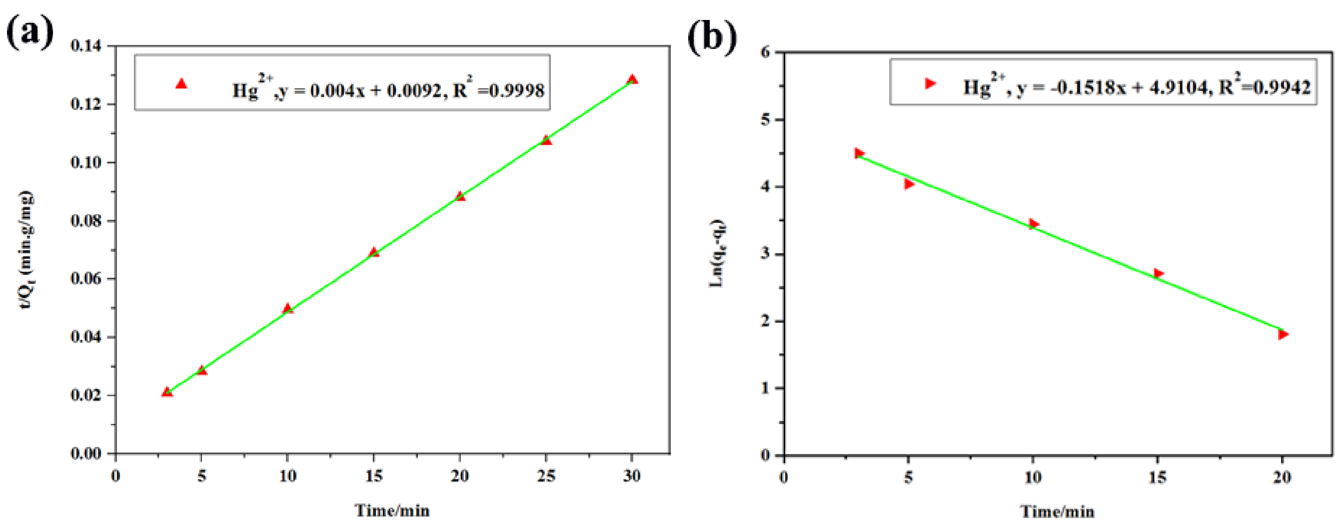

Figure 3. (a) Pseudo-second-order and (b) Pseudo-First-order kinetics models of Hg^{2+} ions adsorption on PCN-221.

Adsorption Isotherm.

Adsorption experiments were carried out by preparing 7 different concentrations (5-10-15-20-25-50-75-100-125 ppm) of mercury ions. Then 10 mg of the adsorbent was added to each solutions and placed in an ultrasonic bath to disperse uniformly for 30 minutes at room temperature. Langmuir and Freundlich models were evaluated for adsorption isotherm.

The correlation coefficient of Langmuir adsorption isotherm was higher than that of Freundlich (R^2 = 0.99), according to the experimental data on the initial concentration of mercury ions, as shown in Table 1. As can be seen in Fig. 4a and b, the maximum adsorption capacity of mercury ions was obtained equal to 277 mg g^{-1}.

Table 1. Langmuir and Freundlich factors for sorption of Hg^{2+} ions.

Langmuir				Freundlich		
adsorbents	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F	n	R^2
PCN-221	233.65	0.507	0.99	76.39	3.017	0.78

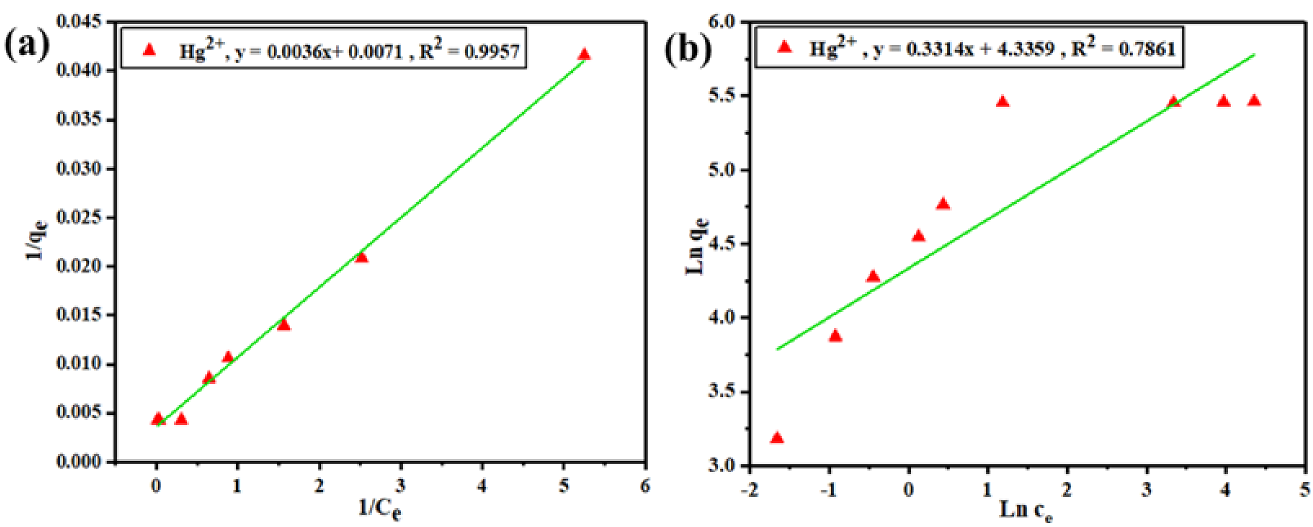

Figure 4. (a) Linear curve fitting with the Langmuir model for Hg^{2+}ions, (b) Linear curve fitting with the Freundlich model.

Investigation of Comparative Adsorption.

The performance of adsorbent PCN-221 was evaluated in the presence of other metal ions. For the comparative experiments, diverse metal ions containing Co^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ni^{2+}, As^{3+}, Fe^{2+}, Cu^{2+}, and Cr^{3+} were prepared, and the adsorption results of these metals are shown in Fig. 5. According to the results, the adsorbent PCN-221 performs fast and efficient toward absorption of mercury metal ions.

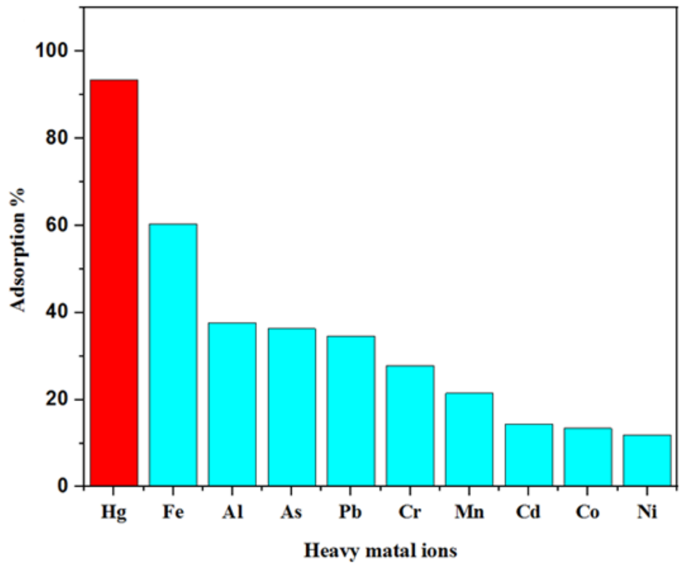

Figure 5. Comparative adsorption of different heavy-metal ions.

Reusability Study.

One of the characteristics of a desirable adsorbent is its reusability in the adsorption process. To investigate this potential of adsorbent PCN-221, the adsorption and desorption cycle of mercury metal ions was performed in three steps. Desorption process was carried out via adding 2 ml of HNO_3 0.01 M to the solution containing mercury ions and adsorbent. After 20 minutes stirring in an ultrasonic bath, the adsorbent was separated by centrifugation and the residual ion was measured using ICP-AES. Satisfactory results are shown in Fig. 6. According to the results, the adsorption percentage in the third recovery cycles indicates the high adsorption capacity of PCN-221 in the adsorption of mercury metal ions.

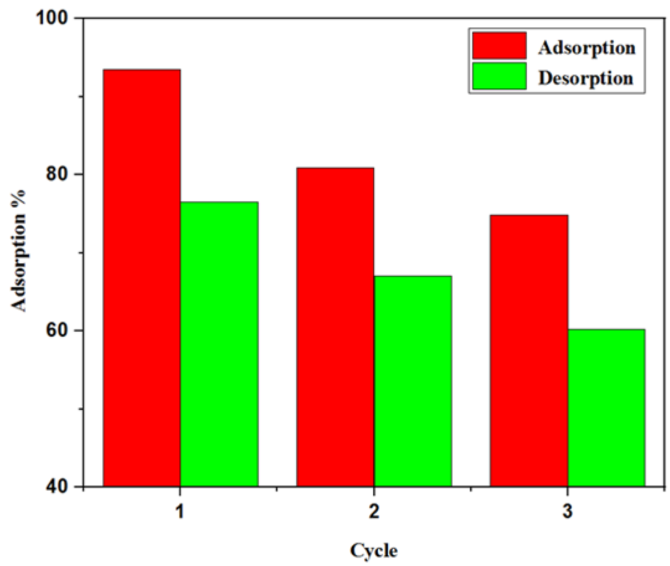

Figure 6. adsorption-desorption cycles of PCN-221.

CONCLUSIONS

In this study, a metal-organic framework namely PCN-221 with porphyrin linkers was synthesized to absorb heavy metal ions from aqueous solutions. The results of adsorption tests showed that the adsorbent illustrates an acceptable performance in adsorption of mercury metal ions. Various parameters such as contact time, metal ion concentration, etc. were evaluated. Absorbent PCN-221 was able to absorb 93% of the mercury metal ions from the aqueous solution and obtain the adsorption capacity of 277, which is relatively high capacities. Moreover, adsorption performance reached to equilibrium in short time under the neutral pH. All these benefits confirm the favorable activity of our proposal framework. The presence of pyrrolic functional sites in the porphyrin linker aids the process of adsorption of mercury ions by the adsorbent and provides an active site for the metal groups. These results show that PCN-221 can be used as an adsorbent to treat water and provide acceptable performance.

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