Removal of lead ion from aqueous solution by Metal Organic Framework

Hossein Shayegan, Yeganeh Davoudabadi Farahani, 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:

Since Pb(II) is one of the toxic water contamination agents, finding an efficient way to remove it from wastewater has become a serious issue in the world. Herein, a metal-organic framework, formulated as (TMU-23), with amide-decorated pores was prepared to investigate its potential in Pb(II) removal performance. At first, various determining factors including pH and adsorbent dosage were optimized. Then, the MOF adsorption capacity was measured about 434.7 mg·g⁻¹. Moreover, reusability feature and effect of competitive cations were checked. Adsorption-desorption tests showed that during three cycles, the MOF could act with favorable efficiency. Modeling calculations illustrate that pseudo-second-order and Langmuir models provide the best description for adsorption mode. Based on these models, monolayer adsorption behavior was responsible for adsorption process through chemical interaction between the analyte and the walls of MOF. Also, the possible adsorption mechanism was examined by exploiting of FTIR spectroscopy, EDS and SEM images. The significant affinity between amide groups of pillars and Pb(II) could cause good removal performance.

Keywords: Heavy metal ions; Metal-organic frameworks; Adsorption; Langmuir; Freundlich.

Introduction:

Recently, metal-organic frameworks, abbreviated as MOFs, have attracted attention worldwide according to their unique features including highly ordered crystalline structure [1], abundant active surface sites [2], tunable pore size [3], high surface area [4] and so forth. MOFs are built from metal-containing units [secondary building units (SBUs)] or metal ions/clusters and organic linkers through making strong bonds [5]. In numerous studies, researchers have examined a wide range of MOFs’ applications including gas storage and separation, molecular recognition, liquid sorption, catalysis and capture of heavy metal ions.

Water contamination agents containing toxic and harmful chemicals have been threatened the human and environmental health [6, 7]. Unfortunately, the development of industry has produced tremendous amounts of wastewater containing heavy metals ions (e.g. Cr³⁺, Ni²⁺, Co²⁺, Mn²⁺ and
Pb\(^{2+}\)). These toxic heavy metals, especially lead(II), is categorized among the non-essential trace elements for biological systems with the maximum permissible levels of 0.015 and 0.01 mg L\(^{-1}\) in potable water based on the Environmental Protection Agency (EPA) and World Health Organization (WHO), respectively [8, 9]. Pb(II) ions release in the environment as a result of radiation device, lead mining, water pipe, battery recycling plants, submarine cable sheathing, electronics assembly plants, solar cell, ceramic, urban rainwater runoff, and paint industries as well as whitening products [10]. Excessive intake of lead(II) will lead to serious illnesses such as lung, kidney, and skin cancers, the nervous and digestive systems damages [11], liver failure, anaemia, nephritis and renal disorders even at a very low concentration. As water is the main carrier of lead ions to human bodies, the decontamination of this cation contaminated wastewater from industrial establishments has become a major challenge. Membrane filtration, chemical precipitation, flocculation, reverse osmosis, adsorption, etc. are some of the routes for removing lead(II) from water. Among these methods and technologies, adsorption is known as a favorable candidate for the purification of wastewater due to environmental friendliness, cost-effectiveness and easy operation. Various adsorbents have been introduced such as active carbon and its derivations, metallogels, LDHs, and polymers [12]. But some disadvantages like complicated preparation, slow adsorption kinetics, difficult regeneration as well as poor efficiency restrict their performance.

**Experimental section:**

Synthesis of bpfb:

1,4-phenylenediamine (1.081g; 10 mmol) was dissolved in 50 ml of dry THF containing 2.84 ml of TEA (20.4 mmol). Then, isonicotinoyl chloride hydrochloride (3.560 g, 20 mmol) was eked into these solutions and heated under reflux for 24 h. The final suspension was filtered, dried under ambient conditions, and poured into an aqueous saturated solution of Na\(_2\)CO\(_3\) (50 ml). The obtained white solid was finally filtered and dried and consumed as the MOF’s pillar.

Synthesis of (TMU-23):

Zn(NO\(_3\))\(_2\).6H\(_2\)O (0.297 g, 1 mmol), H\(_2\)oba (0.258 g, 1 mmol), and bpfb (0.5 mmol) were dissolved in DMF (50 mL) together, then the mixture was sonicated until the reaction was completed (∼30 min) and Red-brown (TMU-23) powders were obtained as pure phases. In the next step, it was washed by DMF, and dried at room temperature as reported in the literature previously [13].

Adsorption Experiments:

In our work, the impact of various parameters on the absorption proficiency of TMU-23 was examined. In this way, 50 ml of lead solution was added to 5 mg of TMU-23 at room temperature and in ultrasonic baths. Pb(NO\(_3\))\(_2\) were utilized as the source of lead ions. The solution pH was controlled via addition of 0.1 ml of 0.1 M sodium hydroxide or 0.1 M HCl. After that, the final mixture was centrifuged for 6 minutes. Finally, sampling from the solution was done.

**Result and Discussion:**
The PXRD patterns of the as-prepared framework conformed to the simulated (derived from the single crystal structures) PXRD patterns (Fig. 1a). Also, Fourier transformed infrared spectroscopy confirmed the correction of the reported synthesis (Fig. 1b).

![Figure 1. (a) PXRD of as-synthesized (red) and simulated (black) TMU-23. (b) FT-IR spectra of TMU-23.](image)

**Pb(II) Adsorption Studies.** Ultrasonic-assisted adsorption of Lead(II) from aqueous solutions were examined by using TMU-23 in order to find the optimal ions initial concentration, pH, contact time, and adsorbent dosage. All experiments were done at room temperature at different conditions, based on the designed experiments.

**Effect of pH.** Absorption procedure relies on the pH strongly. First, 50 ppm of Pb(II) solution was made to examine the absorption behavior of TMU-23. 5 mg of the framework was added to 50 ml of this solution in separate containers. By increasing the pH of the solution, the amount of H⁺ ion declines in the solution and at pH=7, the max amount of lead(II) was adsorbed (Fig. 2).
Study of Sorption Kinetics. To realize the mechanism of the adsorption process, various adsorption models were proposed in literature containing intraparticle diffusion, pseudo-first-order and pseudo-second-order models determining the types of adsorption. TMU-23 adsorption performance followed pseudo-first-order model with a high value of correlation coefficient ($R^2 = 0.994$) (Fig. 3a). Data shows that the chemical adsorption might control the adsorption process of Pb(II) with a more satisfactory correlation compared to the pseudo-first-order model ($R^2 = 0.988$) (Fig. 3b).

Investigation of Comparative Adsorption. In order to investigate the effect of comparative ions on TMU-23 performance, common heavy metals including Co$^{2+}$, Hg$^{2+}$, Cd$^{2+}$, Al$^{3+}$, As$^{3+}$, Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and Cr$^{3+}$ metal cations were selected. As indicated in Fig. 4, our proposal framework adsorbs Pb(II) more efficiently compared to others.
Reusability Study. To check the recyclability of TMU-23, three adsorption-desorption cycles were carried out. The obtained results were collected in Fig. 5. Desorption process was established by adding 2 mL of deionized water to the material, then the solution was stirred for 20 minutes at room temperature. The amounts of total lead(II) were determined by ICP-AES. The percentage of adsorption after three cycles confirmed the reusability of this adsorbent during these adsorption-desorption cycles.

Figure 5. Adsorption-desorption cycles for TMU-23.

Conclusion
In the present study, a metal-organic framework, namely TMU-23, with amide-decorated channels were prepared via utilizing H2oba and bpfb as linkers to check the adsorption performance toward various heavy metal ions. The collected data illustrated that this MOF uptake Pb(II) more efficiently compared to other metal ions. Then, the effects of pH, contact time and adsorbent dosage on adsorption performance of the proposed material were investigated. The adsorption process achieved to the equilibrium less than 15 min which a favorable time for these kinds of adsorbents. At the end of the paper, by using different analyses, including FTIR, EDS, PXRD and SEM images, the mechanism of sorption was presented. We showed that the analyte was adsorbed on the surface of the MOF structure through monolayer chemical interaction.

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