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Mechanistic insight into the interaction and adsorption of Cr(VI) with zeolitic imidazolate framework-67 microcrystals from aqueous solution

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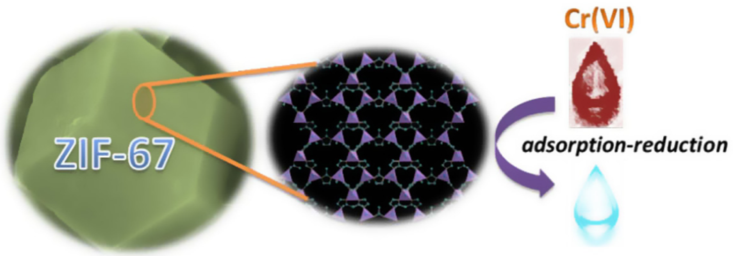
HIGHLIGHTS

- Well-defined rhombic dodecahedral cobalt-based ZIF-67 is synthesized.
- ZIF-67 is explored to remove toxic Cr(VI) in aqueous solution.
- The kinetics and isotherm models of Cr(VI) adsorption on ZIF-67 were studied.
- Cr(VI) removal on ZIF-67 is dominated by electrostatic interaction and ion-exchange mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we report on the synthesis of the well-defined rhombic dodecahedral cobalt-based zeolitic imidazolate framework-67 (ZIF-67) and demonstrate its fast kinetics and high adsorption efficiency towards chromium removal in water for the first time. The ZIF-67 shows good performance for the Cr(VI) removal from aqueous solution. The time needed to reach the equilibrium depends on the relevant initial concentrations, ranging from approximately 20 min for a low initial concentration of 6 mg L^{-1} to more than 60 min for a high initial concentration of 15 mg L^{-1}. The equilibrium adsorption capacities are 5.88, 9.32, and 13.34 mg g^{-1} for 6, 10, and 15 mg L^{-1} of initial Cr(VI) solutions, respectively. The Cr(VI) removal process nicely fits the Langmuir isotherm model and its kinetics follows pseudo-second-order rate equation. The Cr(VI)-adsorbed ZIF-67 is carefully examined by energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), which suggest that the Cr(VI) removal mechanism could be attributed to the electrostatic adsorption of Cr(VI) anions by positively charged ZIF-67 and ion-exchange between the surface hydroxyl groups and Cr(VI), accompanying partial reduction of Cr(VI) to Cr(III) by the reactive framework on the ZIF-67. This work could provide a promising metal–organic framework for the Cr(VI) decontamination in water.

1. Introduction

Currently, the global environment has been polluted significantly by toxic metals owing to the excessive discharge from various industrial, agricultural and mining processes. Chromium (Cr) is a common contaminant in surface- and ground-water, because it is widely applied in electroplating, leather tanning, printing, pigments, polishing, and other industries [1,2]. The Cr(VI) polluted aquatic systems and drinking water sources could increase the risk of severe diarrhea and bladder, liver, kidney, and skin cancers [3], being a serious threat to the environment and human health. Even at relatively low concentrations, Cr(VI) still can cause harm to the human body because of its high toxicity, carcinogenicity and bioaccumulation through the food chain [4]. The United States Environmental Protection Agency (US EPA) set

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maximum contaminant limits for total chromium in drinking water of 100 μg L^{-1} and the World Health Organization (WHO) set a more stricter threshold of 50 μg L^{-1}. To efficiently treat Cr(VI)-containing water and avoid its adverse biological and ecological impacts, considerable attempts have been made for the removal of Cr(VI) based on the implementation of different purification methods [5–9]. Among them, simultaneous Cr(VI) reduction and adsorption is an emerging technique for removal of Cr(VI) pollutants, which not only owns advantage of easy operation, high efficiency, simplicity and cost-effective, but also is favorable for fundamental detoxification of Cr(VI)-contaminated media by transformation of Cr(VI) to Cr(III). Of note, the removal efficiency of such integrated method intimately depends on the characteristic, functionality and ability of the adopted adsorbents, but conventional adsorbents are often failed to fully meet these requirements. Therefore, it is of great importance to explore the new-generation materials with high adsorptivity, affinity and reactivity towards Cr(VI).

Metal–organic frameworks (MOFs) are a new family of nanoporous crystalline materials constructed from metal ions/clusters and coordinated organic linkers, which hold great promise for a variety of applications including gas storage, catalysis, adsorption/separation, drug delivery, luminescence and sensing [10–13]. Intriguingly, the remarkably advantageous features of MOFs, such as flexible structures, tunable pore channels, and intrinsic functionality, endow them with attractive versatility for adsorption-related applications [14–16]. Indeed, several MOFs with various frameworks have been successfully designed and produced as adsorbents for removing various pollutants in water with high efficiency [15,16]. For example, zeolitic imidazolate framework-8 (ZIF-8) made from linking of zinc(II) cations and 2-methylimidazole anions, has been demonstrated the excellent capability towards the effective removal of 1*H*-benzotriazole (BTri) and 5-tolyltriazole (5-TTri) [17] and selective adsorption for theophylline over caffeine and diprophylline [18]. The MIL-101 type of MOFs using terephthalate as organic linkers exhibited the adsorptive performance for the removal of organic dyes in aqueous solution [19,20] and the separation of olefin–paraffin mixtures [21]. Likely, the high-performance adsorption behavior was also observed in carboxylate-linked MIL-100 type of MOFs [22,23]. In comparison to organic contaminants, little attention has been paid on the adsorption of heavy metal using MOFs so far, although the recent studies have shown that the MOFs exhibited good affinity and reactivity towards heavy metals, such as Hg(II) [24], uranium [25,26], and As(V) [27]. Despite these extensive studies on the adsorption application of MOFs in environmental remediation, to a certain extent, it is still not fully understood or very limited on what the adsorption mechanism dominates and how the MOFs interact with heavy metals in water during adsorption process. This is largely due to the uncertainty in the surface composition and structure of the MOFs in the surface-dominated adsorption reaction.

Herein, we report the remarkable adsorption capability of cobalt-based zeolitic imidazolate framework-67 (ZIF-67) towards Cr(VI) removal and experimentally demonstrate how the interaction between Cr(VI) and ZIF-67 to achieve the fast kinetics and high removal efficiency for the first time. The synthesized ZIF-67 with well-defined rhombic dodecahedral morphology is helpful for the fundamental study on the surface-controlled Cr(VI) adsorption process. Based on the characterization of Cr-adsorbed adsorbent, the possible adsorption mechanism of Cr(VI) on ZIF-67 are proposed. These data could provide new insight into the adsorption characteristics of MOFs towards heavy metals.

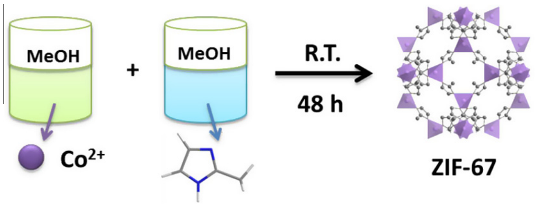

Fig. 1. Schematic illustration of the synthesis of rhombic dodecahedral ZIF-67 microcrystals.

2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate, 2-methylimidazole, methanol, potassium dichromate, 1,5-diphenylcarbazide (DPC) and acetone were obtained from Kelong Chemical Reagent Co. (Chengdu, China). All reagents and chemicals were of analytical grade and used without further purification.

2.2. Synthesis of the rhombic dodecahedral ZIF-67 microcrystals

A schematic diagram of the synthesis procedure is shown in Fig. 1. The rhombic dodecahedral ZIF-67 microcrystals were synthesized according previous report [28]. Typically, 0.249 g of $Co(NO_3)_2{\cdot}6H_2O$ and 0.328 of 2-methylimidazole were dissolved in 25 mL methanol, respectively. The latter clear solution was added into the former pink solution under stirring with a magnetic bar. Stirring was stopped after combining the component solutions. After 48 h, a purple solid was collected by centrifugation, washed with methanol three times and dried at 60 °C for 12 h.

2.3. Characterization

The powder X-ray diffraction (XRD) measurements were performed on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm). The morphology was observed with a JEOL 6700-F scanning electron microscope (SEM). The elemental composition of the samples were characterized by energy-dispersive X-ray spectroscopy (EDS, Oxford instruments X-Max). Surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C, Al KR). All binding energies were calibrated by using the contaminant carbon ($C_{1S} = 284.6$ eV) as a reference. The Fourier transform infrared (FTIR) spectroscopy was recorded on Nicolet 6700 FTIR Spectrometric Analyzer using KBr pellets. The Brunauer–Emmett–Teller (BET) surface area and porous structure were measured using an ASAP 2020 V4.00 G apparatus (Micromeritics Instrument Corp., USA) from the nitrogen adsorption and desorption isotherms at 77 K. The point of zero charge (pH_{PZC}) of the adsorbent was determined by the solid addition method [29,30]. To a series of 100 mL conical flasks, 45 mL of 0.1 mol L^{-1} NaCl solution was transferred. The initial pH values (pH_i) of the solution were adjusted from 3.0 to 13.0 by adding either 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the NaCl solution. Then, 0.1 g of ZIF-67 was added to each flask and the mixtures were agitated at 150 rpm. After 48 h, the final pH values (pH_f) of the solutions were measured. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i. The point of intersection of the resulting curve with abscissa, at which $\Delta pH = 0$, gave the pH_{PZC}.

2.4. Cr(VI) adsorption experiment

The adsorption of Cr(VI) in aqueous solution on rhombic dodecahedral ZIF-67 microcrystals was performed in a batch experiment.