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Ethylenediamine-functionalized cubic ZIF-8 for arsenic adsorption from aqueous solution: Modeling, isotherms, kinetics and thermodynamics

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ABSTRACT

Metal-organic frameworks are novel adsorbents that have been widely used in recent years. The main properties of this emerging adsorbent include high specific surface area, significant porosity, regular structure and adjustable cavities. The main objective of this study was ZIF-8 synthesis with cubic structure, functionalization with ethylenediamine and evaluation for arsenic adsorption from aqueous environments. All the experiments were carried out in batch conditions. Main variables including pH, initial arsenic concentration, adsorbent dosage and contact time were evaluated in this work. In this study, Design of Experiment software was used for experimental runs order arrangement and better understanding of the variables effects on the process. The BET results showed that surface area of the synthesized ZIF-8 and ED-ZIF-8 was 910 m^2/g and 850 m^2/g, respectively. It was also revealed that before and after functionalization with ethylenediamine, ZIF-8 adsorbent was aminined at about 3 mmol/g. In addition, the findings showed that the arsenic adsorption capacity increased from 72 mg/g to 83.5 mg/g. The best pH for arsenic adsorption was neutral (pH ≈ 7). The co-existing of anions effect showed that bicarbonate, sulfate and chloride had the least inhibition effects on arsenic adsorption. This study showed that application of these class of adsorbents can be seriously addressed in solving some environmental challenges.

1. Introduction

Metal-organic frameworks are emerging class of absorbents that have been used extensively. These regular and porous compounds are composed of two main parts. These parts are metal cations and organic linkers [1]. Combining of these two parts in different conditions, can create an amazing compound useable for various fields. Some of their features have high specific surface, significant porosity, regular structure, adjustable cavities [2]. Metal-organic frameworks (MOFs) have various applications such as storage and separation of various gases, transferring of medicine in the patient's body, use as catalyst and adsorbent. One of the most important applications of this new class of materials is their use for pollutants removal from the environment. Of course, in past there application for environmental purification aspects were low, but in last few years, it has significantly increased. These compounds are used to remove some pollutants such as fluoride [2,3], malachite green [4], phosphate [5,6], Pb and Cd [7], Cr(VI) [8] and Hg [9].

One of the most important classes of MOFs is zeolitic imidazole frameworks (ZIFs) [10]. Accordingly, different types of ZIFs adsorbents have been synthesized such as ZIF-8 [11], ZIF-67 [12,13], ZIF-69 [14], ZIF-11 and ZIF-20 [15], ZIF-22 [16], ZIF-90 [17], ZIF-93 [18] and ZIF-95 [19]. ZIF-8 may have different morphologies depending on its synthesis method. So far, different morphologies have been reported for ZIFs including dodecahedral, cubic, and leaf-shaped [20].

There are many pollutants in environment with natural or man-made sources. In the past due to the abundance of water resources, polluted resources were easily ignored. But now, due to some reasons such as climate change and decrease of atmospheric precipitation as well as increase of population growth, this procedure is not reasonable. Therefore, polluted resources should be purified properly. Among various pollutants, arsenic has been considered as a problematic pollutant in some regions [21]. Arsenic is found in both natural and artificial origin in

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water resources [22]. According to the WHO guidelines, the maximum allowable concentration of arsenic is 10 μg/l in drinking water [23,24]. The main objectives of this study were to: First, ZIF-8 synthesis with cubic morphology and its functionalization with ethylenediamine. Second, the evaluation of cubic ZIF-8 and ethylenediamine (ED) cubic ZIF-8 in adsorbing arsenic from aquatic environment.

2. Materials and methods

2.1. Materials

Zinc nitrate hexahydrate, ethylenediamine solution, 2-methylimidazole, ammonium hydroxide, and methanol were supplied by Sigma-Aldrich. All the chemicals used in the experiments applied without further purification.

2.2. Synthesis and post synthetic modification of ZIF-8

Cubic ZIF-8 was synthesized according to previous studies. The solvent used for the preparation of adsorbent in this work was distilled water, which has no harm to the environment [6]. In brief, 0.594 g zinc nitrate hexahydrate and 0.328 g 2-methylimidazole were mixed separately in 3 ml deionized water and 3.76 g ammonium hydroxide solution. After thorough mixing, zinc nitrate hexahydrate solution was slowly added to 2-methylimidazole solution and was stirred for 10 min. After a specified time, a white powder was formed which was separated using a centrifuge. In the next step, after cubic ZIF-8 structure confirmation by XRD and FE-SEM, functionalization process was performed. Before functionalization process, cubic ZIF-8 produced from the previous stage was dried for 24 h at 383 °C. For functionalization, a solution of 30% ethylenediamine was first prepared. Cubic ZIF-8 was placed in a Teflon bottle containing ethylenediamine solution (30%) and put in the oven. The autoclave was heated in an oven at 144 °C for 1 h and then 108 °C for 6 h. Finally, A light-yellow powder was formed which then was separated with a centrifuge. The final powder was washed with distilled water several times. Before the final use the light-yellow powder was dried at of 110 °C for 1 day for activation [25].

2.3. Ethylenediamine-functionalized cubic ZIF-8 nanoparticles

2.3.1. General characterization

The ZIF-8 and ED-ZIF-8 adsorbents characteristics were determined by Fourier Transform Infrared Spectroscopy (Spectrum Two model, PerkinElmer Company), X-ray Diffraction (X' Pert Pro model, Panalytical Company), Energy Dispersive X-ray Spectroscopy, Field Emission Scanning Electron Microscopy (SIGMA VP-500 model, ZEISS Company), and BET surface area and total pore volumes of the samples (BElSORP Mini model, Microtrac Bel Corp.) were determined from nitrogen adsorption isotherms at 77 K.

2.3.2. Adsorption studies

All adsorption experiments were carried out in batch conditions. Initially, the most important variables affecting the adsorption of arsenic were determined through literature review (Table ST-1, Supplementary data). These variables were pH (3−11), initial concentration (1–10 mg/l), adsorbent dosage (1–5 g/l), and contact time (5–60 min). The Design of Experiment software was used to design the experiments. Among the different methods, the Central Composite Design (CCD) method was chosen. According to this method 5 levels were investigated for each variable. The runs and levels of each variable are shown in Table ST (Table ST-2, Supplementary data). All experiments were carried out at the laboratory temperature. In order to provide constant conditions for experiments, the sample volume was considered to be 150 ml for all the experiments. The stirring speed was kept 300 rpm for the experiments. To measure the initial and final concentrations of arsenic, ICP-OES (Instrument Model: Varian VISTA-MPX) was used. Eqs. (1) and (2) were also used to determine the adsorbent arsenic and removal efficiency, respectively [26–28]:

$$q_e = \frac{V(C_o - C_e)}{M} \tag{1}$$

$$R, \% = \frac{(C_0 - C_t)}{C_0} \tag{2}$$

where, q_e (mg/g) is the equilibrium adsorption capacity, C_e is arsenic concentration at equilibrium (mg/l), V is the volume of solution (l) and M is the weight of adsorbent (g). Also, C_0 and C_e are the initial and equilibrium concentrations of arsenic in solution (mg/l), respectively. After obtaining optimum adsorption conditions, isotherms and adsorption patterns were calculated. In this work, Langmuir and Freundlich models were also used to determine the best isotherm model. In addition, pseudo-first-order and pseudo-second-order models were used to determine the best kinetic model [29,30].

3. Results and discussion

3.1. Characterization of as-synthesis ZIF-8 and ED-ZIF-8

The various experiments were carried out to determine the characteristics of the synthesized adsorbents. The XRD shows the crystalline structure of ZIF-8 and ED-ZIF-8. Fig. 1 shows the results of XRD. As shown in Fig. 1, the main peaks of ZIF-8 were very clear and similar to the original sample. The presence of strong peaks indicated good crystallization of the adsorbents. The XRD patterns of ZIF-8 and ED-ZIF-8 were very also similar to each other and have no particular difference. Actually, functionalization has no effect on the crystalline structure of ZIF-8 [25]. the XRD spectra showed that the main peaks were at angles of 2θ between 7, 10.33, 12.8, 14.64, 16.4 and 17.98. Fig. 2 shows the morphology of the synthesized ZIF-8 and ED-ZIF-8. As can be understood from the Fig. 2, ZIF-8 was synthesized into a cubic form. Depending on the synthesis conditions, the ZIF-8 can have different shapes like dodecahedral, cubic, and leaf-shaped [20]. The findings from various studies indicate that the surface area of adsorbents can vary depending on morphology, quality of raw materials and synthesis conditions. Furthermore, the results of BET showed that the surface area of ZIF-8 and ED-ZIF-8 were 910 and 850 m^2/g, respectively. In the Liu et al. [20] surface area of dodecahedral, cubic, and leaf-shaped were 1151.2, 958.4, and 12.7 m^2/g, respectively. After functionalization, the total pore volume was improved. The total pore volume of ZIF-8 and ED-ZIF-8 were 0.57 and 0.65 m^3/g, respectively. The reason for this increase is attributed to the opening of blocked spaces [31]. To analyze the functional groups on ED-ZIF-8, FTIR was used. Fig. 3 shows FTIR results of ZIF-8 and ED-ZIF-8. As shown, the FTIR spectrum of ZIF-8 and ED-ZIF-8 are almost identical, and only in 3381 band a new peak observed which was associated with the N—H group in the ED-ZIF-8. This pattern is consistent with the reference pattern [25]. The results of EDX showed that the percentage of C, N, Zn and O in the ZIF-8 was 49, 22, 27.7, and 1.54, respectively. The percentage of C, N, Zn, and O in the ED-ZIF-8 was 42.54, 30.24, 24, and 3.12, respectively. Also, The results before and after functionalization of ZIF-8 with ethylenediamine showed that the adsorbent was aminined at about 3 mmol per gram of adsorbent. Finally, the arsenic adsorption capacity increased from 72 to 83.5 mg/g of adsorbent (approximately 14% increase in adsorption capacity).

3.2. Statistical analysis and model fitting

The lack of fit (Table ST-3, Supplementary data) showed that the empirical data obtained from arsenic adsorption via ED-ZIF-8 could be described with a polynomial model. As ANOVA results showed (Table ST-4, Supplementary data), the model F value of 41.37 implied that the model was significant. There was only a 0.01% chance for F model