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MIL-68 (In) nano-rods for the removal of Congo red dye from aqueous solution

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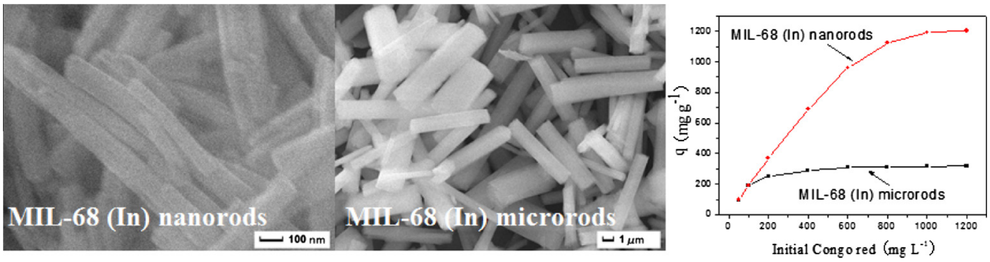
GRAPHICAL ABSTRACT



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ABSTRACT

MIL-68 (In) nano-rods were prepared by a facile solvothermal synthesis using NaOAc as modulator agent at 100 °C for 30 min. The BET test showed that the specific surface area and pore volume of MIL-68 (In) nanorods were 1252 $m^2\,g^{-1}$ and 0.80 $cm^3\,g^{-1}$, respectively. The as-prepared MIL-68 (In) nanorods showed excellent adsorption capacity and rapid adsorption rate for removal of Congo red (CR) dye from water. The maximum adsorption capacity of MIL-68 (In) nanorods toward CR reached 1204 mg g^{-1}, much higher than MIL-68 (In) microrods and most of the previously reported adsorbents. The adsorption process of CR by MIL-68 (In) nano-rods was investigated and found to be obeying the Langmuir adsorption model in addition to pseudo-second-order rate equation. Moreover, the MIL-68 (In) nanorods showed an acceptable reusability after regeneration with ethanol. All information gives an indication that the as-prepared MIL-68 (In) nanorods show their potential as the adsorbent for highly efficient removal of CR in wastewater.

1. Introduction

Water pollution, especially for dyes, has received great attention due to their worldwide application in many industries, such as textile, paper, printing, food, and cosmetics [1]. It is well known that many dyes and pigments are inert, toxic and difficult to biodegrade when discharged into waste streams. In addition to be being a health threat, the presence of dyes and pigments in water is highly visible and affects the water transparency, resulting in reduction of light penetration, and oxygen gas solubility in water [2–4]. Thus, removal of such toxic dyes from the wastewater is a crucial issue.

Metal–organic frameworks (MOFs), as a new class of inorganic–organic hybrid materials based on metal ions coordinated by multidentate organic bridging ligands, have received a great deal of attention because of their attractive potential applications in gas adsorption/separation, catalysis, sensing, drug delivery, and magnetism [5–10]. In the past few years, MOFs have been explored for the adsorption and removal of dyes from aqueous solution, due

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to their diverse compositions and structure types, large surface area, tunable pore size, and coordinatively unsaturated or saturated metal sites to regulate the adsorption ability [11–19]. For example, Jhung et al. reported the liquid-phase adsorption of methyl orange over two typical highly porous MIL-101 (MIL = Material of Institute Lavoisier) and MIL-53 and found that the adsorption capacity of MIL-101 was greater than MIL-53, showing the importance of porosity and pore size for the adsorption [11]. Subsequently, they reported that MOF-235 had high adsorption capacity on the removal of methyl orange and methylene blue from waste water [12]. Yan et al. found that MIL-100 (Fe) gave much higher adsorption capacity for malachite green than other conventional adsorbents such as activated carbon and natural zeolite [13]. Zhang et al. synthesized a heterometallic organic framework material with mixed Ag^+ and In^{3+} ions and found that this target material could rapidly adsorb methyl orange over methylene blue from water in 6 min and release MO in an easy way [14]. Therefore, MOFs are promising candidates as highly-efficient adsorbents in the water treatment.

MOFs in bulk crystal form may restrict their applications in adsorption, catalysis, sensing and drug delivery, because their micropores could prevent large size molecules from entering their internal surface. Nanoscale MOFs with various morphologies and large surface area may show better properties than bulk ones by reducing the diffusion path length [20–22]. Qiu et al. described supramolecular template-directed synthesis of hierarchically mesostructured MIL-101 MOFs and their accelerated adsorption kinetics for methylene blue removal from water [20]. In our past work, we reported solvothermal synthesis of indium-based infinite coordination polymer hierarchical nanostructures and their good adsorption capability for Congo red (CR) dye with a maximum capacity of 577 mg g^{-1} [21]. However, to the best of our knowledge, there have been only few reports on the use of nanoscale MOFs for the removal of toxic dyes from the waste water.

MIL-n materials are a series of MOFs built up with trivalent metal cations such as Al^{3+}, Cr^{3+}, Fe^{3+}, In^{3+} or Ga^{3+} and carboxylic acid under solvothermal synthesis conditions leading to different topological structures, including MIL-68 (In), MIL-53 (Cr), and MIL-101 (Cr). MIL-68 (In) exists in two kinds of the channels with sufficient diameter openings (6 Å and 16 Å), exhibiting high thermal stability and Brunauer–Emmett–Teller (BET) surface area [23,24]. In the present work, we synthesized uniform MIL-68 (In) nano/micro-rods via a facile solvothermal synthesis using NaOAc as modulator agent. The as-prepared MIL-68 (In) nano/micro-rods were used as absorbents for the removal of CR from water. The effects of contact time, dye concentration, solution pH on the adsorption behavior of CR were systemically investigated. Moreover, the adsorption of CR by MIL-68 (In) nano/micro-rods is discussed in terms of kinetics, isotherm and thermodynamics studies.

2. Materials and methods

2.1. Sample preparation

All chemicals are of analytical grade and were used without further purification. MIL-68 (In) nanorods were synthesized according to our previously reported method [25]. In a typical experiment, 2 mmol of $In(NO_3)_3 \cdot 6H_2O$ and 2 mmol of 1,4-benzenedicarboxylic acid (H_2BDC) were added to 20 mL of N,N-dimethylformamide (DMF), followed by addition of 100 μL of 1 M NaOAc (sodium acetate) aqueous solution with vigorous stirring. The resulting reaction mixture was placed in an oil bath (100 °C). After 30 min, the as-obtained precipitates were centrifuged, washed with distilled water and absolute ethanol several times, and dried in vacuum at 60 °C for 5 h. For comparison, MIL-68 (In) microrods were synthesized in the absence of NaOAc, while all other conditions were kept unaltered.

2.2. Characterization

The products were characterized by powder X-ray diffraction (XRD) on a Rigaku D/max 2500PC diffractometer with graphite monochromator and Cu Kα radiation ($\lambda = 0.15406$ nm) at a step width of 0.02°. SEM images and EDS of the products were obtained on a field emission scanning electron micro analyzers (JSM-7001F), employing an accelerating voltage of 5 kV or 20 kV. Nitrogen adsorption–desorption isotherms and surface areas of the samples were measured by the instrument of NOVA 2000e using N_2 adsorption. Prior to the adsorption measurements, the samples were degassed at 200 °C for 10 h under vacuum. The specific surface area was calculated by employing BET method. The pore size distribution and mesopore volume were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. The micropore volume was obtained by *t*-plot micropore analysis. The zeta potential was measured with a Zetasizer Nano Z (Malvern Instruments, UK) at 25 °C.

2.3. Water treatment experiment

In the adsorption kinetics experiment, 20 mg of the as-prepared MIL-68 (In) powder was mixed with 40 mL of aqueous solution of CR with a concentration of 50 mg L^{-1} in a flask reactor (capacity *ca.* 100 mL). The suspension was stirred at room temperature. For a kinetic study, at different time intervals, 4 mL of the solution was pipetted and analyzed after centrifugation (8000 r/min, 5 min). Ultraviolet–visible (UV–vis) absorption spectra were obtained using a UV–vis spectrophotometer (Shimadzu, UV-2550). For the adsorption capacity and thermodynamic study, the initial concentrations of the CR solutions were scaled in the range of 50–1200 mg L^{-1}, and the dosage of MIL-68 (In) samples was kept at 20 mg. All experiments were performed in triplicate. The average values of the results were used and the relative standard deviation was found to be less than 2%. The mixtures were stirred at room temperature for 60 min and centrifugated at 8000 r/min for 5 min. The UV–vis absorption spectra of the final CR solutions were obtained using UV–vis spectroscopy after dilution (if necessary). The concentration of CR was determined using a linear calibration curve from 10 to 50 mg L^{-1} based on the absorbance value at 497 nm.

After the first time it was used, the adsorbent was washed several times, using ethanol by ultrasonication and centrifugation and then dried in vacuum at 80 °C for 10 h. The dried MIL-68 (In) nanorods were reused for adsorption with a CR concentration of 50 mg L^{-1} for 5 min. After each run, the concentration of CR was determined using UV–vis spectroscopy.

3. Results and discussion

3.1. Characterization of MIL-68 (In)

In our experiment, the amount of NaOAc was important in determining the size of MIL-68 (In) rods and the influence of NaOAc was discussed in detail in our previous paper [25]. Fig. 1 shows typical morphologies of the MIL-68 (In) samples. It was observed that the products with the addition of NaOAc were composed of nanorods with diameter distribution of approximately 1.02 ± 0.35 μm in length and 0.12 ± 0.03 μm in width (Fig. 1a and b) and the products without the addition of NaOAc were composed of microrods with diameter distribution of