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Regular Article

Trichloroacetic acid-modulated synthesis of polyoxometalate@UiO-66 for selective adsorption of cationic dyes

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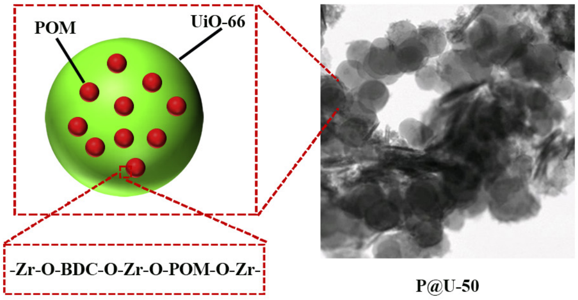
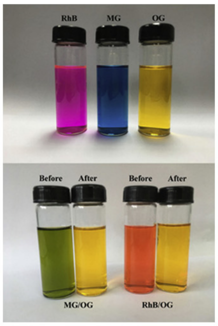
GRAPHICAL ABSTRACT



P@U-50



Selective adsorption of cationic dyes

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ABSTRACT

In this study, POM@UiO-66 nanoparticles were fabricated by encapsulation of POM ($K_6P_2W_{18}O_{62}$ polyoxometalate) into mesoporous UiO-66 metal organic framework through a solvothermal method with trichloroacetic acid as a modulator to promote the defects formation of UiO-66. The as-prepared samples were characterized by TEM, SEM, PXRD, TG, XPS, and EDX elemental mapping, and the successful combination of POM and UiO-66 was confirmed. Two cationic dyes, rhodamine B and malachite green, and one anionic dye orange G were employed to investigate the adsorption performance of POM@UiO-66. The adsorption data showed that the removal process of cationic dyes by POM@UiO-66 matched well with the pseudo-second-order model and Langmuir isothermal model. The resulting POM@UiO-66 nanoparticles exhibited high adsorption to cationic dyes but low adsorption to anionic dyes, and the adsorption capacities of rhodamine B, malachite green, and anionic dye orange G were 222.6, 190.6 and 40 mg g^{-1}, respectively. Furthermore, the cationic dyes could be selectively removed from a cationic-anionic dye binary system. These results suggested that the novel polyoxometalate-based UiO-66 material is a promising candidate for the adsorption of cationic dyes from effluent.

1. Introduction

Organic dyes are widely employed in textile, paper, leather, plastic, rubber, cosmetic, pharmaceutical and printing industries. Dyes are highly visible, even in small amounts, and pose a significant threat to environment and human health due to their toxicity,

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potential mutagenicity and carcinogenicity [1–3]. Thus, removing dyes contaminant from effluent is of significant importance before their discharge. To date, several technologies have been applied for the elimination of dyes from wastewater, such as flocculation, coagulation [4], adsorption [5], advanced oxidation processes [6], photocatalytic degradation [7], membrane filtration [8], and biological treatment [9]. Because of adsorption's high efficiency, easy operation and low cost, this method represents an attractive technology [10]. To date, various types of adsorbents have been developed, such as activated carbon [11], carbon nanotubes [12], zeolite [13], graphene [14], polymeric resin [15], and magnetic adsorbent [16]. However, the design of new adsorbents with high adsorption capacity and selectivity is still desirable.

Polyoxometalates (POMs) are a class of discrete transition metal oxide clusters that are constructed on the condensation of metal oxide polyhedral by a king of self-assembly process. The structures of POMs are diverse, but the most widely studied are the Keggin type ($[XM_{12}O_{40}]^{x-8}$) and Wells-Dawson type ($[X_2M_{18}O_{62}]^{2x-16}$ [17]. POMs with a highly negative charged oxo-enriched surface [18] are expected to exhibit high efficiency and selective adsorption towards cationic dyes. However, the application of POMs as adsorbents is limited because of their solubility in water and polar organic solvent [19]. MOFs are organic-inorganic hybrid solids with infinite and uniform coordination network structure consisting of metal ions/clusters and organic linkers [20]. In virtue of vast surface area, well-ordered crystalline structure, high porosity, multiple coordination sites and modifiable surface properties [21], MOFs have shown various potential applications, such as gas adsorption and storage [22], drug delivery [23], heterogeneous catalysis [24], sensors [25], pollutant elimination [26], and energy storage and conversion [27].

In recent years, selective adsorbents combining the high surface area of MOFs with the high negative charge of POMs have been explored, such as $H_3PW_{12}O_{40}$@ZIF-8 [28] and $K_4PW_{11}O_{40}$@MIL-101 [29]. Based on the thermal and chemical stability, as well as the high surface area, UiO-66, a prototypical zirconium MOF ($Zr_6(OH)_4O_4(BDC)_6$, BDC = benzene-1,4-dicarboxylate) [30], has been one of the most widely investigated MOFs. UiO-66 has two types of mesoporous, tetrahedral and octahedral cages with pore apertures of approximately 8 and 11 Å [31]. Recent works have found that the surface area, crystal shape and size of UiO-66 could be modulated by adding acid in the synthetic mixture to facilitate the formation of defects. The BET surface areas could vary from 1000 to 1890 m^2/g and the sizes of crystal could range from 14 nm to 300 μm [32–37] by altering the pK_a of acid modulator or the amount of acid modulator. Taking the advantages of UiO-66 with enhanced surface area and high adsorption performance of POMs towards cationic dyes, dye adsorbent with high selectivity, as well as large adsorption capacity, could be developed. However, to the best of our knowledge, POM@UiO-66 nanoparticles have not been reported to date.

In this study, new selective adsorbents, POM@UiO-66 (P@U-X), were prepared by combining the high surface area of UiO-66 with the high negative charge of $K_6P_2W_{18}O_{62}$ (POMs) in the condition of defect formation. Trichloroacetic acid with low pK_a (0.64) was chosen as a modulator to promote the formation of defect during the synthetic process. The successful combination of POM and UiO-66 was characterized by TEM, SEM, PXRD, TG, XPS and EDX elemental mapping. Two types of cationic dyes, rhodamine B (RhB) and malachite green (MG), and one anionic dye orange G were employed to perform the adsorption experiments. Moreover, the effect of initial pH on the dye adsorption performance, as well as the adsorption isotherms and kinetics, were investigated. Finally, the selective adsorption of P@U-X towards cationic dye (RhB and MG) and anionic dye (orange G) was discussed.

2. Experimental

2.1. Materials

Zirconium (IV) chloride ($ZrCl_4$), benzene-1,4-dicarboxylate (H_2BDC), and sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). N, N-Dimethylformamide (DMF), ethanol, trichloroacetic acid (TCA), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), rhodamine B (RhB), malachite green (MG), and orange G (OG) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the reagents were used as received without further purification. Ultrapure water (18.25 MΩ cm) was used throughout the study. The stock solutions of dyes (RhB, MG, OG, 500 mg L^{-1}) were prepared by dissolving solid dyes in ultrapure water and kept in the dark. The structures of the different dyes are shown in Fig. 1.

2.2. Preparation of $K_6P_2W_{18}O_{62}$ POM

Dawson-type $K_6P_2W_{18}O_{62}$ was synthesized by the reflux method as reported in Ref. [38] with several modifications. 30 g of $Na_2WO_4 \cdot 2H_2O$ (91 mmol) was dissolved in 30 mL of ultrapure water under vigorous stirring at 50 °C in a three-necked flask. Subsequently, 25 mL of 4 mol L^{-1} HCl (100 mmol) was added into the solution dropwise. After vigorous stirring for 10 min, 25 mL of 4 mol L^{-1} H_3PO_4 (100 mmol) was added into the mixture at 4 drops s^{-1}. Next, the mixture was refluxed at 120 °C for 24 h. After cooling to room temperature, 15 g of KCl (0.2 mol) was added into the solution under vigorous stirring to form a yellow precipitate. Finally, the yellow mixture was subjected to recrystallization and a luminous yellow powder was obtained.

2.3. Synthesis of POM@UiO-66

POM@UiO-66 was synthesized via a solvothermal method. In a typical method, 0.466 g of $ZrCl_4$ (2 mmol) was dissolved in 33 mL of DMF at 70 °C under mild stirring for 1 h. Next, 1.2 g of $K_6P_2W_{18}O_{62}$ was added into the mixture to coordinate with Zr^{4+} for another 1 h. Meanwhile, 0.332 g of H_2BDC (2 mmol) and different equivalents of TCA (0, 5, 10, 20, 50 mmol) (crystals cannot be obtained when excess amount of TCA was added) were dissolved in 23 mL of DMF with continuous stirring at 70 °C for 2 h to form a clear solution. Subsequently, Zr-$K_6P_2W_{18}O_{62}$ solution was mixed with H_2BDC-TCA solution and sonicated for 10 min. Next, the mixed solution was loaded into a Teflon-lined stainless steel autoclave with 100 mL capacity and heated at 120 °C for 24 h. The resulting microcrystalline powders were recovered from the synthesis solutions via centrifugation, sequentially washed with 40 mL of DMF three times and 40 mL of ethanol three times, and stirred at 70 °C for 1 h. The washed products were recovered by centrifugation and dried under vacuum at 85 °C overnight. These nanoparticles prepared in the presence of 0, 5, 10, 20, and 50 equivalents TCA were marked as P@U-0, P@U-5, P@U-10, P@U-20, and P@U-50 respectively.

Defective UiO-66 crystal prepared in the presence of 50 equivalents TCA without $K_6P_2W_{18}O_{62}$ was marked as U-50. UiO-66 was prepared using the same method without adding $K_6P_2W_{18}O_{62}$ and TCA.

2.4. Characterization

The morphology of the nanoparticles was observed by Hitachi H-7000FA transmission electron microscopy (TEM) with an accelerating voltage of 100 kV and scanning electron microscopy (SEM) (Zeiss, Germany) with a voltage of 20 kV. Ultraviolet–visible