Materials Research Bulletin 83 (2016) 387–395

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Synthesis of nano-porous Bi_2WO_6 hierarchical microcrystal with selective adsorption for cationic dyes

Danjun Wang[a,*], Jie Zhang[a], Li Guo[a], Xinbo Dong[b], Huidong Shen[a], Feng Fu[a,*]

[a] College of Chemistry &Chemical Engineering, Yan'an University, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan'an 716000, PR China
[b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry, Department of Chemistry (Ministry of Education), Northwest University, Xi'an 710069, PR China

ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form 15 May 2016
Accepted 19 June 2016
Available online 20 June 2016

Keywords:
A. Nanostructures
A. Inorganic compound
B. Chemical synthesis
B. Solvothermal
C. X-ray diffraction
D. Surface properties

ABSTRACT

Novel three-dimensional spherical porous-Bi_2WO_6 microcrystals were synthesized *via* a facile hydrothermal method. In order to investigate its adsorption properties, three kind of dyes, such as rhodamine B(RhB), methyl-blue(MB) and methyl-orange(MO) were selected as model pollutant to evaluate its preferential adsorption property. The static adsorption test shows that the as-prepared spherical porous-Bi_2WO_6 microcrystal possesses higher adsorptivity for the adsorption of MB than that of RhB and CR. According to a series of dynamic and thermodynamic analysis, the adsorption process conforms to the pseudo-second-order kinetic model and Langmuir isotherm model well. Furthermore, adsorption property of RhB, MB, MO, AR, Ph, p-NPh and 2,4-DNPh on Bi_2WO_6 was also compared and a plausible mechanism of the preferential adsorption property of three-dimensional spherical porous-Bi_2WO_6 microcrystal was also discussed according to its structure. It is believed that the as-prepared porous-Bi_2WO_6 microcrystal may provide potential applications in environmental fields.

1. Introduction

During the past few decades, a large amount of wastewater containing dyes and pigments have been discharged into the aquatic environment with the rapid development of modern industry, which will lead to devastating consequences on our daily life and living condition [1]. As known to all, printing and dyeing wastewater has special properties, such as complex composition, high chemical oxygen demand value (COD), high colority and is difficult to be degraded [2–7]. Recently, various physicochemical and biological treatment technologies, such as coagulation, precipitation, filtration, oxidation, activated sludge and adsorption process have been employed to remove dyes from aqueous solutions [6,8–10]. Among these technologies, adsorption the pollutants onto the surface of absorbent is an important physicochemical mechanisms governing a wide range of environmental processes and it arouses extensive interest for its low cost, facile experimental condition and easy to be recycled [11–16].

[17–22]. As one of the most important Bi-based materials, Bi_2WO_6 has attracted a lot of attentions because of its excellent intrinsic physical and chemical properties, such as ferroelectric piezoelectricity, catalytic behavior, and nonlinear dielectric susceptibility [23–26]. Furthermore, it may be possess high adsorptivity due to its orthorhombic structure which is constructed by alternating $(Bi_2O_2)^{2+}$ layers and perovskite-like $(WO_4)^{2-}$ layers [23]. There are huge repulsive force between $[WO_4]^{2-}$ octahedrons, and the same is true between $[Bi_2O_2]^{2+}$ layers, which decides that Bi2WO6 is easy to form layer structure in the reaction [23–26]. The novel lamellar structure provides many pores and large specific surface area with the more adsorption sites. Generally speaking, sorbate molecules with low chemical affinity with the outer sites show a reaction-limited adsorption and diffuse to the inner sites. For the reaction-limited adsorption, sorbet molecules diffuse to the inner sites in a short time, while the adsorption process mainly occurs inside the sorbate. Conversely, it leads to a diffusion-limited adsorption, for which adsorption to the outer sites accounts for the instantaneous first phase of adsorption and is followed by an increasingly slower adsorption [26,27]. In addition, Bismuth is known as a kind of green elements, BiIII-based oxides is widely used as drug, ceramics and and catalysis [28,29]. So, BiIII-based oxides adsorbent is duitable for the removal of environmental pollutants.

* Corresponding authors.
E-mail addresses: wangdj761118@163.com (D. Wang), FengFu@163.com (F. Fu).

http://dx.doi.org/10.1016/j.materresbull.2016.06.029
0025-5408/

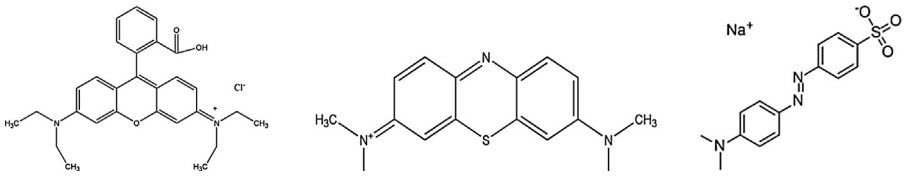

Fig. 1. Molecular structure of the kind of dyes: RhB(left), MB(middle) and MO(right).

[21]. Furthermore, Ag and AgBr nanoparticles were deposited on the surface of Bi2WO6 via a following facile photoreduction process and precipitation-deposition method, respectively. The photocatalysis experimental results reveal that Ag nanoparticles loaded on the surface of Bi_2WO_6 can significantly enhance its photocatalytic activity [22]. In this contribution, we fabricated the novel three-dimensional spherical porous-Bi_2WO_6 microcrystal via a facile hydrothermal process. For the first time, we report our investigation in utilization of porous-Bi_2WO_6 as adsorbent with high selectivity for removal of MB from aqueous solutions. Various factors, including the initial dye concentration, adsorbent dosage and the initial pH of the solution, which effect the adsorption processed was also investigated. The adsorption equilibrium isotherms and kinetics were also evaluated. The experimental results demonstrate that as-synthesized porous-Bi_2WO_6 exhibits significantly enhanced selectivity adsorption properties for removal of dye and easy to be recycled. Furthermore, the adsorptive mechanism was also discussed.

2. Experimental section

2.1. Synthesis of 3D Bi_2WO_6

Sodium hydroxide (NaOH), bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), $Na_2WO_4{\cdot}2H_2O$ and nitric acid (HNO_3) were analytical grade and used without further purification. Deionized water was used throughout the experiments. In a typical process, 0.9704 g $Bi(NO_3)_3{\cdot}5H_2O$ was first dissolved in 6.0 mL of nitric solution (4.0 mol L^{-1}), and then, the above solution was added drop-wise to 10 mL aqueous solution containing 0.6529 g of $Na_2WO_4{\cdot}2H_2O$ under vigorous stirring. Under stirring, the diluted NaOH (1.0 mol L^{-1}) was used to adjust the pH value to 3. After being magnetically stirred at room temperature for 2 h, the resulting precursor suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 190 °C for 12 h. Subsequently, the autoclave was cooled to room temperature naturally. After filtration, the yellowish white precipitate was collected and washed with distilled water and ethanol for several times, then dried under vacuum at 60 °C for 4 h.

2.2. Characterization

The purity and crystalline structure of the samples were carried out with a Shimadzu XRD-7000 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.15418 nm). The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5400 X-ray spectrometer. The morphology of the sample was observed by the field emission scanning electron microscopy (FE-SEM, JSM-6700F). The samples were further investigated by high-resolution transmission electron microscopy (HR-TEM). HR-TEM studies were carried out on a JEM-2100 electron microscope at an acceleration voltage of 200 kV. The selected area electron diffraction (SAED) pattern was obtained from HR-TEM to determine whether the sample is single crystalline. The pore diameter distribution and specific surface area of Bi_2WO_6 architectures were tested by nitrogen adsorption-desorption (Automated Physisorption and Chemisorption Analyzer, Micrometritics ASAP 2010).

2.3. Organic dye solution selective adsorption

Three kind of ionic dyes, such as rhodamine B (RhB^+), methylblue (MB^+) and methyl-Orange (MO^-), were used as the simulated pollutants to investigate the charge and size of the pollutants affect the adsorption efficiency. MB^+ and MO^- have the charge effect due to the similar size but different charge, while MB^+ and RhB^+ have the same charges but different molecular sizes. Its structure is shown in Fig. 1. A series of adsorption-desorption experiments were carried out at 25 °C. The initial dye concentration, the sorbent dosage and pH value of the dye solution were investigated. The change of absorbance of dye was followed its λ_{max} as a function of adsorption time and the removal rate was calculated. For comparison, activated carbon and cationic resin (Hebei Huozhong Co., Ltd.) were employed to evaluate the potential performance for wastewater treatment. During the adsorption, 5 mL solution was taken at given time intervals and then the Bi_2WO_6 sorbent were separated through centrifugation. The supernatant was decanted and the absorbance of dye was determined through its maximum adsorption band using Shimadzu 2550 UV–vis spectrotometer and the absorption of maximum peak was monitored. The adsorption capacity of the sorbent was determined as formula:

$$q_t = (C_0 - C)\cdot V/m, \quad (1)$$

where C_0 is the initial concentration of the dye solution(mg L^{-1}), C is the dye concentration after adsorption (mg L^{-1}), V is the volume of dye solution(20 mL), m is the weight of sorbent (g). The kinetic models we used are shown in Table 1. The amount of dye adsorbed onto the sorbent when the adsorption reached to equilibrium (q_e, mg g^{-1}) was determined by Formula (1), where c_e is the residual dye concentration at equilibrium. The adsorption isotherm models we used are shown in Table 2.

3. Results and discussion

3.1. Crystallinity, morphology and porous structure

The phase structure, crystallinity and purity of as-obtained samples were examined by XRD and XPS. The XRD patterns are shown in Fig. 2. The diffraction peaks at 2θ of 28.3°, 32.8°, 32.9°, 47.0°, 47.1°, 55.8°, 58.5°, 68.7°, 75.9° and 78.5° can be perfectly indexed to orthorhombic Bi_2WO_6 (JCPDS file No.39-0256),

Table 1
The adsorption kinetic models.

Theoretical models	The formulation
Lagergren pseudo-first-order kinetics model	$\ln(q_e - q_t) = \lg q_e - \frac{k_1}{2.303}\cdot t$
Pseudo-second-order kinetic model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2}k + \frac{1}{q_e}\cdot t$
Intraparticle diffusion model	$q_t = k_p \cdot t^{0.5} + c$

Note: ❶ q_e q_e means the equilibrium adsorption quantity of adsorbate on unit absorbent, unit, mg g^{-1}; q_t: unit adsorption quantity on unit absorbent; t: adsorption time; k_1: the apparent adsorption rate constant of the agergren preudo-first-order kinetics model, min^{-1}; ❷ k_2 k_2: the apparent adsorption rate constant of pseudo-second-order kinetic model, mg g^{-1} min^{-1}; k_p: the apparent adsorption rate constant intraparticle diffusion model.