Journal of Cleaner Production 184 (2018) 949–958

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Size-selective adsorption of methyl orange using a novel nano-composite by encapsulating HKUST-1 in hyper-crosslinked polystyrene networks

Jiachun Shen [a], Xuzeng Wang [a], Limin Zhang [a, **], Zhen Yang [a, b, *], Weiben Yang [a], Ziqi Tian [d], Jianqiang Chen [c, ***], Tao Tao [b]

[a] School of Chemistry and Materials Science, School of Environment, Jiangsu Provincial Key Laboratory of Material Cycling and Pollution Control, Nanjing Normal University, Nanjing 210023, PR China
[b] Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Nanjing University of Information Science & Technology, Nanjing 210044, PR China
[c] College of Biology and the Environment, Nanjing Forestry University, Nanjing 210037, PR China
[d] Department of Chemistry, University of California, Riverside, CA 92521, United States

ARTICLE INFO

Article history:
Received 3 November 2017
Received in revised form
1 March 2018
Accepted 2 March 2018
Available online 2 March 2018

Keywords:
Size-selective adsorption
Polystyrene networks
HKUST-1
Theoretical calculation
Ionic dyes

ABSTRACT

A novel nano-composite adsorbent, NDA88-Cu, was successfully prepared by immobilization of HKUST-1 (a typical MOF) into hyper-crosslinked polystyrene networks NDA88 (loading ratio: 350 mg of MOFs with particle size in the range of 10–100 nm per gram of polystyrene networks). The adsorbent demonstrated advantages of improved stability without leakage of metal ions during the adsorption assays compared to HKUST-1 itself, and faster solid-liquid separability than NDA88 or HKUST-1, which could effectively avoid the shortcomings of MOFs like potential secondary pollution and poor performance in separation. When applied for the adsorption of five typical dyes with various charges and molecular sizes (cationic: methylene blue (MB) and rhodamine-B (RhB); anionic: methyl orange (MO), methyl red (MR) and acid green (AG25)), NDA88-Cu worked for the removal of anionic ones but showed almost no adsorption capacity towards cationic ones because of Donnan membrane effect exerted by the host NDA88. For the three anionic dyes, NDA88-Cu displayed not only heightened adsorption capacity towards MO (398.8 mg/g), but also size-selective uptake of MO from solution with mixed dyes. The adsorption capacity remained high levels after ten adsorption-desorption cycles. Mechanism investigations, including macroscopic physico-chemical analyses, instrumental investigation and density functional theoretical calculations, gave direct evidences of the size selectivity of NDA88-Cu with hierarchical pore structure. Coordination effect of Cu-MO predominated, while π-π interactions and electrostatic attraction also took place, in the fixing of MO onto the adsorbent. The current work provides a useful idea for the separation of contaminants with similar structure from water, and acts as a good case for the application of nanotechnology in wastewater treatment and resource recovery.

1. Introduction

Large amount of dye-contaminated wastewater has attracted increasing attention. Generally, dyes are aesthetically unfavorable and cause annoyance to the aquatic biosphere (Jung et al., 2017). Many dyes are even toxic and carcinogenic at very low concentrations. Therefore, removal of dyes from water is of vital significance. Among various methods for the removal of dyes from water, adsorption gains its superiority for effectivity, easy operation, environmental-friendliness, and regeneration of adsorbents (Elwakeel et al., 2012; Li et al., 2009; Sathishkumar et al., 2012; Szyguła et al., 2008). Especially, during the regeneration process, valuable resources adsorbed, treated as contaminants in water, are possible to be recycled (Kloepfer et al., 2005). However, other

* Corresponding author. School of Chemistry and Materials Science, School of Environment, Jiangsu Provincial Key Laboratory of Material Cycling and Pollution Control, Nanjing Normal University, Nanjing 210023, PR China.
** Corresponding author.
*** Corresponding author.
E-mail addresses: zhanglimin@njnu.edu.cn (L. Zhang), yangzhen@njnu.edu.cn (Z. Yang), chenjq@njfu.edu.cn (J. Chen).

https://doi.org/10.1016/j.jclepro.2018.03.015
0959-6526/

coexisting dyes with similar structures or properties may also be adsorbed, engendering difficulty for separation of targeted resources in later desorption process (Donia et al., 2008). If all these dyes are adsorbed but not able to be separated, it is actually a waste of resources. Thus, exploring adsorbents with high selectivity for separation of one dye from other dyes with similar structures is necessary.

Plenty of attention have been given to metal-organic frameworks (MOFs) (Farrusseng et al., 2009; Ferey, 2008; Lin et al., 2015), which is one sort of crystalline porous nano-materials with huge surface area (James, 2003; Yaghi et al., 2003). The application of MOFs in environmental remediation, especially in wastewater treatment as adsorbents, has also been investigated (Hasan et al., 2013; Khan et al., 2013; Wang et al., 2015; Zhuo et al., 2017). Despite the reported fascinating adsorption capacities of the nano-materials, the use of MOFs in water pollution control is limited by several factors, including their relatively poor stability in water, difficulty in solid-liquid separation and potential secondary pollution (Li et al., 2013). Immobilization of the nano-particles into large-sized porous matrix materials is expected to provide an approach to overcome the above limitations (Jawad et al., 2017). In our previous work, we successfully synthesized novel composite beads by encapsulating MIL-101(Cr) into sodium alginate and chitosan hydrogels. The products could effectively remove organic contaminants from wastewater and avoid previous shortcomings (Zhuo et al., 2017). However, the obtained beads in the form of hydrogels are with relatively poor mechanical strength for practical use.

Polymeric adsorption resins, which own characteristics of high mechanical strength, large adsorption capacity and feasible regeneration for recycling (Blaney et al., 2007; Huang et al., 2013; Perondi et al., 2012), such as the famous commercial hyper-crosslinked anion exchanger NDA88 (structure shown in Fig. 1a), with plentiful inner meso-/micro-pores and primary amino groups, can be selected as suitable matrix, because of the following potential advantages: (i) $-NH_2$ groups can act as anchors to fix metal atoms of MOFs (Chen et al., 2013); (ii) The resin itself possesses high adsorption capacity for anionic contaminants, and the potential Donnan membrane effect exerted by protonated −NH2 groups could enhance the permeability and pre-enrichment of target anionic pollutants from bulk solution to inner surface of the adsorbent, which is also expected to enhance adsorption of anionic contaminants (Cumbal and SenGupta, 2005; Pan et al., 2013; Sarkar et al., 2010); (iii) More importantly, if MOFs are assembled in the inner pores of resins, the controllable hierarchical pore structure of the nano-composite is expected to provide extra size-selectivity in the adsorption of certain contaminants. Various sorts of commercial resins like NDA88 have been widely employed in both fundamental study and industrial application, and have been proved to possess good stability with few mass loss after repeated use, as polystyrene is known to be hardly degradable. To the best of our knowledge, such hybrid materials formed by immobilization of MOFs into polymeric adsorption resins in water treatment application are rare up to now.

In this study, a new nano-composite adsorbent, marked as NDA88-Cu, was prepared by a facile method in which nano-sized MOFs, HKUST-1, was structured in the inner pores of NDA88 to overcome the original drawbacks of MOFs. Structural characterization, as well as stability and solid-liquid separability tests, of the novel nanocomposite, was performed to demonstrate the improvement in practical application compared with HKUST-1. Five typical dyes with various charges and sizes (cationic: methylene blue (MB) and rhodamine-B (RhB); anionic: methyl orange (MO), methyl red (MR) and acid green (AG25)) that could cause significant environmental and health problems, including skin irritation and biological metabolism disturbance, were employed to assess the adsorption performance. Among them, MO and MR, two azo dyes, are well known carcinogenic organic substances (Gupta and Suhas, 2009; Wan et al., 2017). The novel adsorbent showed not only high adsorption capacity toward MO, but also enhanced selective separation and recovery of MO from mixed-dye wastewater. Moreover, to clarify the adsorption mechanism, macroscopic physico-chemical analyses, instrumental investigation and theoretical calculations based on density functional theory (DFT), were performed.

2. Materials and methods

2.1. Materials

1,3,5-benzenetricarboxylic acid (H_3BTC) and $Cu(NO_3)_2 \cdot 3H_2O$ were purchased from Energy Chemical Co. Ltd (P. R. China). NDA88 was purchased from Jiangsu N&G Environmental Technology Co. Ltd (P. R. China). All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd (P. R. China). Deionized water was utilized in all experiments.

2.2. Synthesis of NDA88-Cu

The nano-composite adsorbent was prepared by a facile method as illustrated in Fig. 1a: NDA88 (1g) and $Cu(NO_3)_2 \cdot 3H_2O$ (24 g) were added into water (500 mL). The mixture was mechanically stirred for 48 h at 25 °C to ensure that Cu(II) ions were loaded on NDA88. Afterwards, the resin beads loading Cu(II) were filtered, washed by water for 3 times, and then dispersed into a H_3BTC solution where 2.5 g of H_3BTC was dissolved in ethanol-water solution (250 mL of ethanol and 50 mL of water). The mixture was heated to 85 °C for 12 h in water bath. Finally, the nano-composite was filtered, washed by water-ethanol (volume ratio of 1:1) solution for 3 times, and dried in an oven. The product was NDA88-Cu. According to the thermogravimetric analysis, the loading ratio of the nano-composite is 350 mg HKUST-1 per gram of polystyrene networks.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2500VL/PC X-ray diffractometer at a voltage of 40 kV and a current of 30 mA using Cu Kα radiation. XPS spectra were characterized on a ULVAC-PHI 5000 VersaProbe XPS spectrometer. Scanning electron microscopy (SEM) images were recorded by a JEOL JSM-5610LV SEM with an acceleration voltage of 25.0 kV. Zeta potential (ZP) was measured on a Malvern Nano-Z Zetasizer. BET specific surface areas were determined on a Micromeritics ASAP-2010C automatic analyzer with N_2 as the adsorbate. Cu ions concentration was determined by an Agilent AA240 atomic absorption spectrophotometry.

2.4. Batch adsorption experiments

Adsorption experiments were conducted in 150-mL conical flasks. 100 mL of dye aqueous solution with specific initial concentration and pH (adjusted using 0.1 moL/L HCl or NaOH aqueous solution) was added into the flask. The dye solution in each flask was treated by 50 mg of adsorbents. All flasks were placed in an incubator shaker with a constant shaking speed (140 rpm) at room temperature (25 °C) to make sure the well dispersibility of adsorbents throughout the whole process.

After adsorption, the concentrations of dyes of the supernatants were measured by a Hitachi UH5300 UV−vis spectrophotometer. To avoid the impact of pH on adsorption spectra, all dye samples were diluted by 2.4 mol/L of HCl aqueous solution before